THE
PRINCIPLES

THEORETICAL CHEMISTRY,

WITH SPECIAL REFERENCE TO THE

CONSTITUTION OF CHEMICAL COMPOUNDS.

BY

IRA REMSEN,
PROFESSOR OF CHEMISTRY IN THE JOHN HOPKINS UNIVERSITY.

FOURTH EDITION,
THOROUGHLY REVISED.

LONDON:
BAILLIÈRE, TINDALL, & COX.
PHILADELPHIA: LEA BROTHERS & CO.
1893.

PREFACE TO THE FOURTH EDITION.

In preparing this new edition I have been tempted to change the book fundamentally and give it a character more in keeping with the recent tendencies of work in the field of Physical or General Chemistry. But, taking everything into consideration, I have concluded to resist the temptation, and remain true to the original title and character of the book. Accordingly, it is essentially what it has been—a brief treatise on those facts and speculations that have to deal especially with the problem of the constitution of chemical compounds. My object has been and is to help students to get clear ideas in regard to the foundations of chemistry. That the treatment has been regarded with favor is shown by the fact that four editions of the book have been demanded in a comparatively short time; and, further, by the fact that, since the appearance of the last American edition, it has been translated into German

and into Italian. I believe that all changes called for by the advance of the science have been made, and that this edition will be found abreast of the times. The chief addition is a short Chapter on Solutions.

IRA REMSEN.

BALTIMORE, September, 1892.

CONTENTS.

CHAPTER I.

PAGE

INTRODUCTION 13

CHAPTER II.

COMBINING NUMBERS—ATOMIC WEIGHTS—ATOMIC THEORY . 19

Law of definite proportions—Dalton's investigations—Law of multiple proportions—Atomic theory—Determination of atomic weights—Method for the determination of atomic weights dependent upon analysis—Equivalents—Determinations by Berzelius—The principle of substitution employed in the determination of atomic weights—Consideration of chemical decompositions for the purpose of determining atomic weights — Elements — Compounds — Mechanical mixtures—Solutions and alloys.

CHAPTER III.

EXAMINATION OF GASEOUS ELEMENTS AND COMPOUNDS . . . 34

Investigations of Gay Lussac—Avogadro's views—Determination of molecular weights—Number of atoms in the molecules of elements—Molecules of elements which contain more or less than two atoms—Varying number of atoms in the molecule of one and the same element—Other proofs of the fact that the molecules of elements contain more than one atom—Molecular formulas of gaseous compounds—Apparent exceptions.

CHAPTER IV.

A STUDY OF SOLUTIONS 60

Relation between the vapor-pressure of solutions and the molecular weights of the dissolved substances—Relation between the freezing-points of solutions and the molecular weights of the dissolved substances—Relation between the osmotic pressure of solutions and the molecular weights of the dissolved substances—Exceptions to the laws of solutions.

CHAPTER V.

PAGE

EXAMINATION OF SOLID ELEMENTS AND COMPOUNDS 65

Specific heat—Relations between specific heat and atomic weight—Investigations of Dulong and Petit—Investigations of Neumann and Regnault—Determination of atomic weights by a study of the specific heat of compounds—Exceptions to the law of Dulong and Petit—Isomorphism as furnishing a means for determining atomic weights.

CHAPTER VI.

PROPERTIES OF THE ELEMENTS AS FUNCTIONS OF THEIR ATOMIC WEIGHTS—THE PERIODIC LAW 78

Natural groups of elements—Mendelejeff's tables—Lothar Meyer's arrangement of the elements.

CHAPTER VII.

VALENCY 88

Definition — Name of the new property—Distinction between valency and affinity—Methods for determining the valency of the elements—Is valency constant or variable?—Variation of valency towards one and the same element—Atomic and molecular compounds—Foundation for the distinction between atomic and molecular compounds—Use of the distinction—Difficulties met with—Experiments showing that nitrogen may be both trivalent and quinquivalent—The distinction between atomic and molecular compounds unnecessary as far as the hypothesis of valency is concerned—Saturated and unsaturated compounds—Maximum valency and apparent valency—Maximum valency is dependent upon conditions—Are all the bonds of an element of the same order—Self saturation of atoms—Single, double, and triple linkage of atoms of the same kind—Relative valency—Periodic variations in valency—Classification of the elements with reference to their valency—Application of the views concerning valency to the study of chemical compounds.

CHAPTER VIII.

CONSTITUTION OR STRUCTURE OF CHEMICAL COMPOUNDS—DEFINITION OF CONSTITUTION, ETC. 111

Definition, etc.—Linkage of atoms.

CHAPTER IX.

PAGE

Constitution of Classes of Compounds 120

Acids—Hydrogen acids—Hydroxyl acids—Sulphur acids—Nitrogen acids—Double halogen acids—Classification of acids—Bases—Differences between acids and bases—Complex bases—Salts—Complex salts—Anhydrides—Experimental evidence of the constitution of anhydrides—Oxides—Analogy between salts and anhydrides and oxides.

CHAPTER X.

Constitution of Classes of Compounds of Carbon . . . 136

Hydrocarbons—Homologous series—Alcohols—Classes of alcohols—Primary alcohols—Secondary alcohols—Evidence in favor of the general formula of secondary alcohols—Tertiary alcohols—Mercaptans—Acids—Methods for the formation of acids of carbon—Aldehydes—Acetones—Ethereal salts—Ethers—Anhydrides.

CHAPTER XI.

Constitution of Substitution Products 161

Substitution products containing chlorine, bromine, or iodine—Complex substitution products—Constitution of substituting groups—Constitution of the group CN—Constitution of the group SO_3H—Constitution of the group NO_2—Constitution of the group NO—Constitution of the group NH_2—Constitution of the group NH—Constitution of the groups N_2H_3 and N_2H_2.

CHAPTER XII.

Special Study of the Constitution of Chemical Compounds 175

Compounds not containing carbon, or inorganic compounds: Compounds of chlorine, etc., with oxygen, and with oxygen and hydrogen—Compounds of sulphur, etc., with oxygen, and with oxygen and hydrogen—Sulphurous acid—Sulphuric acid—Pyrosulphuric acid—Thiosulphuric acid—Dithionic acid—Trithionic acid—Tetrathionic acid—Pentathionic acid—Compounds of nitrogen with oxygen, and with oxygen and hydrogen—Hydroxylamine—Compounds of phosphorus with oxygen, and with oxygen and hydrogen—Hypophosphorous acid—Phosphorous acid—Phosphoric acid — Pyrophosphoric acid —Metaphosphoric acid—Compounds of boron with oxygen, and with oxygen

PAGE

and hydrogen—Compounds of silicon with oxygen, and with oxygen and hydrogen—General remarks on the relations of ordinary acids to the so-called normal acids—Salts—Ammonium salts—Salts of copper and mercury—Salts of iron and chromium—Salts of aluminium—Metal acids—Compounds of uranium.

CHAPTER XIII.

CONSTITUTION OF CARBON COMPOUNDS 199

Methane derivatives (Fatty compounds); Compounds derived from the hydrocarbons C_nH_{2n+2}—Derivatives of ethane—Isomerism—Derivatives of propane—Derivatives of butane—Derivatives of pentane—Derivatives of hexane—Derivatives of heptane.

CHAPTER XIV.

MONOBASIC ACIDS, $C_nH_{2n}O_2$, ETC. 211

Propionic acid—Butyric acids—Valeric acids—Caproic acids—Aldehydes—Acetones or Ketones—Diacid alcohols, $C_nH_{2n+2}O_2$—Monohydroxy-monobasic acids, $C_nH_{2n}O_3$—Hydroxy-propionic acids—Lactones—Dibasic acids, $C_nH_{2n-2}O_4$—Triacid alcohols and tribasic acids—Glycerin—More complex alcohols and acids—Cyanogen compounds—Mustard oils—Derivatives of carbonic acid.

CHAPTER XV.

UNSATURATED COMPOUNDS ALLIED TO THE MARSH-GAS DERIVATIVES 229

Ethylene and derivatives—Propylene, etc.—Alcohols—Acids—Acetylene—Compounds containing a smaller proportion of hydrogen.

CHAPTER XVI.

BENZENE DERIVATIVES. (AROMATIC COMPOUNDS) . . . 238

Constitution of benzene—Substitution products of benzene—Di-substitution products—Tri-substitution products—Peculiar benzene derivatives—Phenols—Quinones—Azo- and diazo-compounds—Azoxy- and hydrazo-compounds—Phenylmethanes—Rosaniline and pararosaniline—Phthaleins—Phenylethylene — Furfuran—Pyrrol—Thiophene—Naphthalene—Pyridine and quinoline—Anthracene—Retrospect.

CHAPTER XVII.

PAGE

PHYSICAL METHODS FOR THE DETERMINATION OF THE CONSTITUTION OF CHEMICAL COMPOUNDS 274

General — Specific volume—Molecular refraction — Methods dependent upon determinations of the amount of heat evolved in chemical reactions or thermal methods—Heat of formation—Heat of neutralization—Magnetic rotary polarization in relation to chemical constitution—The shape of molecules.

CHAPTER XVIII.

THE STUDY OF CHEMICAL AFFINITY 290

Introduction—The nature of the problem—Rough measurements of affinities—Disturbing influences—Attempts to measure affinity by observations on the heat evolved in chemical reactions—Resultant affinity—Heat of neutralization—Avidity of acids—Mass action—Measurement of coefficients of affinity—Volume-chemical method—Specific coefficient of affinity—Methods for determining specific coefficients of affinity.

CHAPTER XIX.

CONNECTION BETWEEN THE CHEMICAL CONSTITUTION AND PROPERTIES OF COMPOUNDS 302

General—1. Change of character in certain parts of a compound caused by the introduction of some atom or group—Bases, alcohols, acids—Influence of acid groups like NO_2—Change in the chemical character of ammonia—Influence of the nitro group on chlorine—Substitution in Hydrocarbons—Oxidation phenomena—2. Tendency on the part of certain compounds to break down in certain ways—Anhydrides—Lactones—Lactams and Lactims—Other anhydro-compounds—Elimination of carbon dioxide—Conclusions warranted by the facts just presented—Breaking down of unsaturated compounds—3. Influence exerted by certain atoms or groups in a compound on the constitution of the products formed by further acts of substitution—Substitution in symmetrical compounds—Influence of acid or negative groups on groups of the same kind—Influence of basic or positive groups—Regularities in the addition of negative or acid atoms to unsaturated compounds—4. Relative ease with which isomeric compounds enter into action—Decomposition of halogen derivatives.

nized was *the law of the indestructibility of matter.* It was found as the result of many observations that the sum of the masses of the products of a chemical change is always exactly equal to the sum of the masses of the substances which act upon one another. Nothing is gained or lost in the operation. This law, like every other law of nature, is simply a statement of what has been found to be true in every case that has been studied, and its statement implies that a large number of cases have been studied. Since its truth was first recognized, an almost infinite number of observations have confirmed it in the most striking way. As regards the question whether it is possible to conceive of a state of things in which the law of the indestructibility of matter would not hold good we have nothing to do. It may be said, however, that the law could not have been discovered without the aid of many quantitative chemical experiments. It is an expression of facts established. It is not an axiom.

The next law discovered was *the law of definite proportions;* and almost at the same time came *the law of multiple proportions.* These two laws are the expressions of the facts learned in studying the proportions in which the elements combine with one another.

The discovery of a law naturally leads to a desire to explain it. When we have recognized that elements combine according to the laws of definite and multiple proportions, we next ask, Why do they combine in this way? An attempt to answer this question leads to some suggestion which is known as an *hypothesis.* If, after it has been thoroughly tested by further extensive study of the facts, the hypothesis is found to be in harmony with all the facts, and capable of explaining them, it is then called a *theory.* The *atomic hypothesis* was put forward to explain the laws of definite and multiple proportions, and this hypothesis has proved of great value in enabling chemists to deal with the facts of chemistry. It has long since been accepted as a satisfactory theory.

Besides the laws mentioned several others bearing upon the proportions by weight or by volume in which substances act upon one another have been discovered, and all have been found to be explicable by the aid of the atomic hypothesis. Among them may be mentioned the law of combination by volume, the law of specific heats, and,

most comprehensive of all, the periodic law, based upon a recognition of the fact that the properties of the elements are functions of their atomic weights, that the properties of any element are determined by its atomic weight.

Again, laws governing the complexity of chemical compounds have been discovered. It has been found that there is a law that limits the number of atoms of one element which can combine with one atom of another. A careful consideration of the facts upon which this law is based has led to certain conceptions in regard to the structure or constitution of all chemical compounds; and it has been found that, by a study of the transformations and of the methods of formation of compounds, definite conclusions regarding their structure can be reached. Similarity of structure is found to be the cause of similarity of properties. By studies on the constitution of chemical compounds a rational classification of chemical reactions was made possible, and the study of these reactions was very much simplified.

Up to the present most chemical investigations have had for their object the determination of the constitution of compounds and much still remains to be done. Indeed, but little more than a beginning has been made in this direction. Much more exact studies are called for in many cases, and most of the laws governing the connection between constitution and chemical reactions are still undiscovered. We are beginning the quantitative period in the study of constitution. The results thus far achieved are of such importance that we may confidently look forward to still further great advances—perhaps greater than those already recorded.

The main object in view in this book is to point out as clearly as possible the reasons for accepting the prevailing views in regard to constitution, to show that these views are not merely products of the imagination, but that they are the legitimate results of a profound and comprehensive study of chemical phenomena, and that they are the simplest views possible, if we accept as the basis of speculation the atomic theory. Whatever fate may await the prevailing theories it is certain that the facts expressed in our present chemical formulas must find expression in their successors. The formulas of the future will express all

the facts expressed by the formulas of the present, besides others yet to be discovered.

Just as chemical studies have shown that similarity in chemical conduct implies similarity in constitution, so studies on the physical properties of compounds have shown that similarity in constitution is connected with similarity in certain physical properties, and the further investigation has been pushed along this line, the closer has this connection appeared to be. It is in this direction that we must look for more definite views in regard to constitution than we have at present. Chemists are now engaged very largely in classifying chemical compounds according to their reactions without having any clear conception or any hypothesis in regard to the physical structure of the simplest chemical compounds. And yet, though we have no hypothesis in regard to the physical structure of chemical compounds, it requires no argument to convince us that every chemical compound has a definite physical structure; and the discovery of the structure of any one compound would give us an insight into all chemical compounds. If now, as investigation is pushed farther and farther, it can be shown that certain physical properties always accompany a certain chemical constitution, we may finally be able to interpret our views regarding structure in physical terms. A brief chapter of this book is devoted to a presentation of those methods which have been of most service in showing a connection between physical properties and chemical constitution.

However important the study of the constitution of chemical compounds may be, and no one doubts its great importance, there is much to be learned regarding chemical phenomena, besides the constitution of the substances which take part in a reaction. We might know the constitution of every compound,—there would still remain important questions to be answered. The one great question is, What is the cause of chemical action? We may in the same way be thoroughly acquainted with the phenomena of the motion of the heavenly bodies and of falling bodies without having any conception in regard to the cause of these phenomena. We may be familiar with the phenomena of light and not know the cause of these phenomena; and so with the phenomena of heat and sound, and electricity and magnetism. As regards the

cause of the phenomena of the motion of the heavenly bodies and of falling bodies we have no conception at the present day. It is true, we say that these phenomena are caused by the attraction of gravitation, and certain laws governing this attraction have been determined, and if we assume that all bodies are pulled together by a force which is proportional to the masses of the bodies, and inversely proportional to the squares of the distances, we have an explanation of the phenomena; but, after all, we do not know what pulls these bodies together. The phenomena of heat and of sound have found a much more satisfactory explanation in the suggestion that they are due to the rapid motion of the bodies themselves, or of the small particles of which the bodies are believed to be composed. In the mechanical theory of heat we have probably the most satisfactory theory put forward to account for a class of natural phenomena. Not many years ago heat phenomena were explained by assuming that there was a substance, *caloric*, which could be put into substances and taken out of them.

As regards the question, then, What is the cause of chemical action? no satisfactory answer can be given. Indeed, in most of the investigations which have thus far been carried on, no attempt has been made to answer it. These investigations have had to do almost entirely with questions of composition and constitution. What are the substances brought together, and what are the substances found? have been the main questions asked; and but little attention has been given to the action itself. The changes brought about have been ascribed to the action of a special force, called *chemical affinity;* a force which was considered to have its seat in the atoms, and to act between atoms in somewhat the same way that the attraction of gravitation is considered to act between masses. From time to time attempts have been made to learn more in regard to the nature of this force. At one time chemical attraction was regarded as essentially identical with electrical attraction; again, it was regarded as identical with the attraction of gravitation. Both of these views have been shown to be untenable. Of late this subject has received considerable attention, and in the work that has been done there is much promise. Studies have been made on the velocity of various chemical reactions;

on the influence of mass on chemical action; on chemical equilibrium; on the influence of temperature on the course of chemical reactions, and various other phenomena, a detailed knowledge of which is necessary, in order that a satisfactory theory of chemical affinity may be framed. A brief chapter will be devoted to an account of the chief results obtained in investigations on chemical affinity. In this chapter there will be some reference to the connection between heat phenomena and chemical action, but no attempt will be made to treat the subject of thermochemistry in anything but the broadest outlines, notwithstanding the fact that work in this field has been carried on with great industry for twenty years past, and many results have been attained which are of importance in the study of chemical phenomena. So far as these results have a direct bearing upon the subject of chemical constitution, or upon the nature of chemical affinity, they will receive attention.

From what has been said, it will be clear that we have as yet no theory of chemical affinity, as we have a theory of heat. We simply think of it as an attractive force exerted between atoms. We are just at the beginning of the study of the laws of chemical affinity, a knowledge of which must precede the formation of any clear conception of the force. The time may come when we shall have a theory of chemical affinity, in the light of which all chemical phenomena will appear much simpler than they do now, just as all heat phenomena find a ready explanation in the mechanical theory of heat. This theory of affinity will be an extension of our present atomic theory—it will have to do with the action of atoms, and not merely with their existence in a condition of equilibrium; in other words, it will deal not alone with the *statical* side of chemical phenomena, but with the *dynamical*.

CHAPTER II.

COMBINING NUMBERS—ATOMIC WEIGHTS—ATOMIC THEORY.

Law of Definite Proportions.—The first fundamental law governing all transformations of matter is, as has been stated, the law of the indestructibility of matter. Next in order of discovery came the law of definite proportions. According to this:—

Every chemical compound always contains the same constituents in the same proportion by weight.

This law, though perhaps tacitly acknowledged by most chemists, was not fully established until the beginning ot the present century. In 1803 a strong effort was made by Berthollet, in his work entitled *Statique Chimique*, to show that the law is not true, but the opposition called forth by this work, particularly from Proust, led to more and more careful examinations of chemical compounds, and thus to the firm establishment of the law. Proust also showed that two elements can combine with each other in more than one proportion, and that for each compound thus formed the proportions of the constituents are fixed.

Dalton's Investigations, Law of Multiple Proportions.—In the year 1804 Dalton's investigations enabled him to take another advance step. Another general law governing chemical action was discovered and propounded. This is the *law of multiple proportions*. As this is of fundamental importance, it will be well to follow, somewhat in detail, Dalton's reasoning. Many substances had been analyzed before his time, and the percentages of the constituents had been determined with a fair degree of accuracy. He examined, first, two gases, both of which consist of carbon and hydrogen, viz., olefiant gas and marsh-gas. He analyzed them both, and determined the percentages

of the constituents contained in them. These percentages are as follows:—*

Olefiant gas,	85.7 per cent. carbon,	and	14.3 per cent. hydrogen.
Marsh-gas,	75.0 " "		25.0 " "

On comparing these numbers, he found that the ratio of carbon to hydrogen in olefiant gas is as 6 to 1; whereas, in marsh-gas it is as 3 to 1, or 6 to 2. The weight of hydrogen, combined with a given weight of carbon, is exactly twice as great in the one case as in the other.

For the two oxides of carbon, further, the following figures were obtained:—

Carbon monoxide,	42.86 p. c. carbon,	and	57.14 p. c. oxygen.
Carbon-dioxide,	27.27 "		72.73 "

But 42.86 : 57.14 : : 6 : 8, and 27.27 : 72.73 : : 6 : 16.

The weight of oxygen, combined with a given weight of carbon in carbon dioxide, is exactly twice as great as the weight of oxygen combined with the same weight of carbon in carbon monoxide. He saw, again, that, in olefiant gas, one part by weight of hydrogen combines with six parts by weight of carbon, and that, in carbon monoxide, eight parts by weight of oxygen combine also with six parts by weight of carbon. Water was now examined. It contains 88.89 per cent. oxygen and 11.11 per cent. hydrogen, and these numbers are to each other as 8 to 1. The numbers which, in the first place, represent the combining proportions of oxygen and hydrogen, respectively, with carbon, are also found to represent, in the second place, the combining proportions of oxygen and hydrogen with each other. Subsequent examination of other compounds led to similar results, and thus Dalton had discovered the law of multiple proportions. This may be stated as follows:—

If two substances, A and B, form several compounds with each other, and we consider any fixed mass of A, then the different masses of B, which combine with this fixed mass of A, bear a simple relation to each other.

This law has been fully confirmed by all investigations which have been carried on since the time of Dalton.

* Instead of the figures actually found by Dalton, the corrected figures are given, for the sake of simplicity.

Atomic Theory.—But Dalton did not stop with the discovery of the law of multiple proportions; he sought for its explanation. He was thus led to propose the *atomic hypothesis*, as affording the simplest explanation of the facts observed.

The question as to the ultimate constitution of matter had frequently and from the earliest dates been discussed. Two views were held at different periods, and by different thinkers. According to one of these, matter was supposed to be indefinitely divisible; according to the other, it was supposed that there is a limit to the divisibility, and that this limit is reached when the division has been carried to certain small particles called *atoms*. After the discovery of the law of multiple proportions, however, the atomic theory acquired a more definite form, as the existence of atoms was supposed to have a direct connection with chemical combinations. The results of Dalton's investigations are not fully stated in the law of multiple proportions as above given; another fact was made clear, which is also of importance. The complete results may be stated as follows: It was shown that for each element a particular number might be selected, and that this number, or a simple multiple of it, represents the proportion by weight in which this element combines with other elements. This is a fact, which involves no hypothesis regarding the nature of matter. The "combining numbers" of the elements may be used without reference to or thought of the existence of atoms. But the question naturally suggests itself: Why do elements combine according to the laws of definite and multiple proportions? No absolute, final answer can be given to this question, but we can imagine a cause, or, as it is commonly expressed, we can propose an hypothesis. This Dalton did. He supposed that chemical action takes place between atoms, *i. e.*, between particles that are indivisible and have definite weights. If chemical combination takes place between one atom of one substance and one atom of another substance, or between a simple number of atoms of one substance and a simple number of atoms of another, and these atoms have definite weights, then, indeed, the explanation of the laws of definite and multiple proportions is given.

Thus the idea of atoms became a much more tangible one than it had been up to that time. Not only were

atoms supposed to have definite weights, but a method was suggested by means of which their relative weights could be determined. The number assigned to an element, representing its combining weight, also represents the relative weight of its atoms. The fact that the combining weight of an element was in some cases represented by a multiple of the simplest number was satisfactorily accounted for by supposing that in these cases more than one atom of the element combined with one of another element.

Determination of Atomic Weights.—The determination of combining numbers or atomic weights, as the figures were indiscriminately called by some, became now the chief, immediate problem of the science of chemistry. Dalton's atomic hypothesis was accepted by many, though not by all. The laws governing chemical combinations could not be doubted, but the explanation could be and was. Nevertheless, the importance of determining for each element the characteristic number, call it atomic weight or combining weight, or combining number, was acknowledged by all; and consequently particular attention was given to this field of research during the period directly following the time of Dalton's publication. Let us see how thoroughly the desired object could be accomplished by the aid of the principles laid down by Dalton.

At the time of which we are speaking, the methods for chemical analysis were still far from perfect, and hence most of the determinations then made required subsequent corrections which were gradually made as analytical methods were improved. This fact has, however, nothing to do with the subject under consideration. The principle alone is involved. The question to be answered is: Can the relative weights of the atoms be determined by the method used by Dalton? To decide this question we must first examine the method more carefully. In the following discussion, the correct numbers, as given by later analyses, are employed, instead of those originally found. This does not interfere with the principle, and does simplify the subject otherwise.

Method for the Determination of Atomic Weights dependent upon Analysis.—As the standard the combining

weight of hydrogen was first selected, and this made 1. Hydrogen combines with oxygen in the proportion of 1 : 8; and as water was the only compound of hydrogen and oxygen known, the conclusion was drawn that the two elements were united in the simplest way; that is to say, one atom of the one element to one of the other, and hence the atomic weight of oxygen is 8. Further, nitrogen is combined with hydrogen in ammonia in the proportion of one part by weight of hydrogen to $4\frac{2}{3}$ parts by weight of nitrogen. Ammonia was the only compound of nitrogen and hydrogen known; and the same reasoning as that above employed led to the conclusion that the atomic weight of nitrogen is $4\frac{2}{3}$. Considering for a moment these two simple cases, we see that the numbers thus found, as representing the relative weights of the atoms of oxygen and nitrogen, are founded partially upon hypothesis. There is nothing to decide as to the number of atoms of hydrogen and oxygen contained in water, nor of nitrogen and hydrogen in ammonia, and, of course, as long as this number is unknown, it is impossible to draw a positive conclusion with reference to the atomic weights of nitrogen and oxygen. A conclusion to be of value must be based upon a thorough knowledge of the compounds of the particular element under consideration. Such a number must finally be selected as is most in accordance with the facts. The selection must remain more or less arbitrary, as can be shown more clearly.

Take again the case of oxygen. A second compound of hydrogen and oxygen is now known. This contains the elements in the proportion 1 : 16. At first sight, the explanation of this appears simple enough. In this second compound there are two atoms of oxygen combined with one of hydrogen, and thus the proportion is satisfied. But may we not with equal right decide that in water there are two atoms of hydrogen combined with one of oxygen? This would give us for oxygen the atomic weight 16, and, in the second compound, there would be one atom of each of the elements.

Further, if the attempt be made to determine the atomic weight of carbon by Dalton's method, difficulties fully as great are encountered, and the final selection among many numbers must be more or less arbitrary. Taking olefiant gas, we have hydrogen combined with carbon in the pro-

portion 1 : 6; in mars[illegible]s the proportion is 1 : 3 or 2 : 6. If we [illegible] in olefiant gas the elements are [illegible] atom, then the atomic weight of [illegible] consequently in marsh-gas there must be two atoms of hydrogen combined with one atom of carbon. But here again it can just as well be assumed that in marsh-gas there is the simplest kind of combination, and this would give 3 for the atomic weight of carbon. Then in olefiant gas two atoms of carbon would be combined with one atom of hydrogen.

Finally, let us take the oxygen compounds of carbon. In carbon monoxide, carbon is combined with oxygen in the proportion 6 : 8 or 3 : 4, whereas in carbon dioxide the corresponding proportion is 6 : 16 or 3 : 8. Now let us suppose the atomic weight of oxygen to be 8. Then, if carbon monoxide is the simpler of the two compounds, the atomic weight of carbon is 6; and in carbon dioxide there are two atoms of oxygen combined with each atom of carbon. Here, again, it is evident that carbon dioxide may just as well be assumed to be the simpler compound, in which case the atomic weight of carbon would be 3, and in carbon monoxide there would be two atoms of carbon combined with one atom of oxygen. Between these different possibilities it is impossible to decide with the aid of the knowledge obtained by analyses. The number of similar instances might be multiplied indefinitely; the inadequacy of the method could be made more strikingly clear by examples of a more complicated kind, but the cases mentioned are sufficient for the purpose; we must have other methods for the determination of atomic weights before we can get numbers which are not more or less arbitrary.

Equivalents.—This necessity was first clearly recognized by Wollaston in 1814. As no satisfactory method for the determination of atomic weights suggested itself, he proposed to abandon the idea of atomic weights entirely, and to substitute for it that of the *equivalent*, thus, as he supposed, getting rid of all hypotheses and obtaining numbers that were simple expressions of facts. The equivalent of an element was to him that quantity of the element that possessed the same chemical value as a given quantity of another element, that quantity of an element that could take the place of a given quantity of

another element. According to the conditions of this definition, it is plain that, in order to know what portions of two elements are equivalent, we must be able to compare the two. Hence, primarily, only of such elements as can be compared with each other, of such as possess a certain degree of similarity, can the equivalent quantities be determined. As this direct comparison is not always, nor, indeed, in the majority of cases, possible, recourse must be had to indirect comparison.

To illustrate this let us take an example: Hydrogen and chlorine combine with each other in the proportion of 1 part by weight of hydrogen to 35.4 parts by weight of chlorine, and from this fact the conclusion is drawn that 35.4 parts of chlorine are equivalent to 1 part of hydrogen. In the same way it is found that 8 parts of oxygen, 80 of bromine, 16 of sulphur, are all equivalent to 1 part of hydrogen. Knowing that 35.4 is the equivalent of chlorine, the quantities of sodium and silver that are respectively equivalent to this quantity of chlorine are now determined. For sodium 23 is found, and for silver 107.7. These quantities of silver and sodium are further found to be equivalent to 8 parts of oxygen, 79.8 parts of bromine, and 16 parts of sulphur, and hence the conclusion is drawn that they are also equivalent to 1 part of hydrogen. Thus the equivalents of sodium and silver have been determined by the method of indirect comparison. In most simple cases this method of procedure is justifiable, but it must be distinctly borne in mind that such numbers as are determined by indirect comparison with the standard, whatever this may be, are not in the strictest sense expressions of facts; the last step in the determinations, however justified we may be in taking it, requires, nevertheless, the aid of hypothesis.

But if the difficulty thus referred to were the only one met with in the determinations of equivalent numbers, such determinations would have nearly the full value claimed for them by Wollaston. This, however, is not the case. As soon as any but the simplest compounds are involved, we are left in fully as much doubt in regard to the equivalent numbers as we are in regard to atomic weights. If it be required to determine the quantity of carbon that is equivalent to 1 part of hydrogen, the compounds of the two elements must be examined. But there are a great

many compounds of these two elements. Taking but two, olefiant gas and marsh-gas, it is found that in the former (see *ante*, p. 24) 1 part of hydrogen is combined with (equivalent to) 6 parts of carbon; whereas, in the latter, 1 part of hydrogen is combined with (equivalent to) 3 parts of carbon. What shall here decide which is the correct number? It is evident from such instances as this that the idea of the equivalent is fully as uncertain as that of the atom was at the time of Wollaston. That an element could be equivalent to two entirely different quantities was in itself paradoxical if the original definition of equivalent was retained. These difficulties seem not to have been apparent to Wollaston. He continued his determinations of equivalents, and during this time a fusion of the ideas of equivalent and atomic weight took place unconsciously. As neither of these ideas was then definite, as to each of a number of elements a number of atomic weights could be assigned, and almost as many equivalents, the succeeding period in the history of chemistry was *one of great confusion*, and it finally became evident that some new idea or ideas must be introduced, if a firm foundation for the science was to be reached.

Determinations by Berzelius.—Before the necessary new ideas were introduced, the methods at hand were employed to the full extent. All known compounds of any given element were compared with each other, and a number finally selected, that best satisfied the facts, to represent the equivalent of the element, or its atomic weight, as it was called by others. Berzelius attacked the subject most successfully. He laid down rules, by the aid of which, according to him, the number of atoms of an element contained in a compound could be determined, and hence also its atomic weight. Then, by more careful analyses than had been previously made, the atomic weights or equivalents of all the elements were determined. A large number of these determinations depended upon chemical rules, similar to the following, given by Berzelius:—

> *If an element forms several oxides, and the quantities of oxygen contained in them, as compared with a fixed quantity of the element, are to each other as* 1 : 2, *then it is to be concluded that the first compound*

consists of one atom of the element and one atom of oxygen; the second, of one atom of the element and two atoms of oxygen (or two atoms of the element and four atoms of oxygen). If the ratio is 2 : 3, then the first compound consists of one atom of the element and two atoms of oxygen: the second of one atom of the element and three atoms of oxygen, etc.

This rule covers those cases in which it is required to determine the atomic weight of an element by a study of its oxides. Other rules were given, in which sulphur compounds, etc., were made the basis of calculation.

It will be observed that, although in these rules the oxygen and sulphur are taken as the elements, the number of whose atoms varies, the other elements might just as well be taken, and the atomic weights obtained would then be entirely different. An example will make this clear: Mercury combines with oxygen in two proportions. In the first compound, 8 parts of oxygen are combined with 199.8 parts of mercury; in the second, 16 parts of oxygen are combined with 199.8 parts of mercury. Adopting the rule above laid down, we should conclude that in the first compound 1 atom of mercury is combined with 1 atom of oxygen, and, in the second, 1 atom of mercury with 2 atoms of oxygen. If, then, 8 is the atomic weight of oxygen, 199.8 is the atomic weight of mercury. But if, on the other hand, the quantity of oxygen be regarded as remaining fixed, and that of the mercury as varying, then we should have in the first compound 8 parts of oxygen combined with 199.8 parts of mercury, and, in the second, 8 parts of oxygen combined with 99.9 parts of mercury; and, by a similar process of reasoning, the conclusion could be drawn that the first compound contains 2 atoms of mercury to 1 atom of oxygen, and the second, 1 atom of mercury to 1 atom of oxygen, and thus we should obtain 99.9 as the atomic weight of mercury instead of 199.8 as found above. Berzelius had made certain observations on chemical compounds upon which he based his rules, but, as we shall see, these observations were not sufficient.

Another difficulty presented itself in the case of those elements that combine only in one proportion with oxygen. What should decide in regard to the number of atoms of oxygen contained in a compound of such an element?

Here speculation was the only aid, and it often led to false results.

The Principle of Substitution employed in the Determination of Atomic Weights.—The researches of Berzelius added much to the knowledge of the combining weights of the elements, and the determinations made by him undoubtedly rested upon a firmer basis than the determinations made previously. He made the fullest and most logical use of purely chemical means that could be made at the time. Subsequently, however, a new fact was discovered in connection with chemical compounds, that proved of great value in simplifying the consideration of chemical phenomena, and also aided materially in the solution of the problem of the determination of atomic weights. This is *substitution*. A brief explanation will suffice here to show the connection between this subject and the problem under discussion. It has been found that certain elements have the power of entering into compounds, driving out some of the constituents. For instance, water contains two atoms of hydrogen and one of oxygen; if potassium be allowed to act upon water, a portion of the hydrogen is given off, and a new compound containing both potassium and hydrogen, in addition to the oxygen, is the result. If now potassium be further allowed to act upon this new compound, the hydrogen contained in it is driven out, and potassium enters. Thus we obtain from water, by replacing its hydrogen by potassium, a compound containing two atoms of potassium and one atom of oxygen. This kind of action is called *substitution*.

To show how, by taking into account the transformations included under this head, conclusions of importance may be drawn with reference to atomic weights, one example will suffice: It has been seen that the chief difficulty in determining atomic weights or equivalents by chemical means lies in the lack of data for estimating the number of atoms of an element contained in any given compound. Take the case of marsh-gas. In it 1 part of hydrogen is combined with 3 parts of carbon, and, as above stated, from this fact the conclusion might be drawn that the atomic weight of carbon is 3. If, however, it can by any means be proved that the number of atoms of hydrogen contained in the gas is greater than one, the conclusion

would require modification. By means of the process of substitution, this can be proved, or at least it can be proved that the hydrogen contained in marsh-gas can be subdivided, and, hence, if we accept the atomic hypothesis, it follows that the compound contains in its smallest part more than one atom of hydrogen. By allowing chlorine to act upon marsh-gas, a portion of the hydrogen is replaced, and a compound containing hydrogen and chlorine is formed. This new compound treated with chlorine again gives up a portion of its hydrogen, and takes up chlorine in its place. This operation can be repeated four times, and thus finally a compound is obtained which contains only carbon and chlorine. Each time the same proportion of hydrogen is given up, and is replaced by an equivalent quantity of chlorine. Thus it is plain that the hydrogen originally contained in marsh-gas is divisible into four parts, and it follows that there are at *least* four atoms of hydrogen contained in marsh-gas—a conclusion which could not possibly be reached by the aid of the means heretofore considered. If now that quantity of carbon which is in combination with four atoms of hydrogen is assumed to be one atom (and, by a consideration of the whole list of carbon compounds, this step is justified), then the atomic weight of carbon is 12. The method, thus briefly illustrated, is capable of application to some extent, but not to such an extent as to render it a general method for the determination of atomic weights.

Consideration of Chemical Decompositions for the purpose of determining Atomic Weights.—One other method of reasoning must be referred to as having been employed, either for the purpose of furnishing proofs of the correctness of atomic weights determined by other means or for the direct determination of these weights. An example will best make this matter clear. It is desired to know, for instance, how many atoms of hydrogen are combined with nitrogen in ammonia; or, having by the preceding method concluded that this number is 3, we wish to test the conclusion by other observations. By treating nitric acid (which we will suppose to contain one atom of hydrogen to every atom of nitrogen) with hydrogen ammonia is obtained. Now, it is found that, when a given quantity of nitric acid is converted into ammonia, in the

resulting ammonia, three times as much hydrogen is combined with the same quantity of nitrogen. Further, ammonia combines directly with a number of compounds, and an examination of the quantity of hydrogen contained in this ammonia shows that it must necessarily be represented by three or some multiple of three atoms of hydrogen. Thus, a study of the various cases in which ammonia is either formed or destroyed, or enters into combination, always shows that the quantity of ammonia thus playing a part must contain three or some multiple of three atoms of hydrogen; and hence it appears that in ammonia at least three atoms of hydrogen are combined with each atom of nitrogen.

The methods which have thus been briefly described comprise all at our command for the determination of atomic weights dependent upon purely chemical processes. Consider these methods as we may, it is obvious that they are inadequate to the accomplishment of their object. The determinations may indeed be made, but there must always remain a doubt concerning the result. If, then, the problem can be approached from an entirely different point of view, this doubt will be reduced to a minimum, if it is found that the results first obtained assert themselves as correct in the second instance. Before passing, however, to the presentation of new methods for making these determinations, it will be well to apply the knowledge thus far gained in fixing as definitely as possible the conceptions of elements and compounds.

Elements.—An element, strictly speaking, is a substance that cannot by any possible means be decomposed into kinds of matter that are unlike in their chemical properties. This definition presupposes a knowledge of all possible means of decomposing substances. Until we are positive that we are acquainted with all these means, we cannot be positive in regard to the existence of a single element. But it is plain that to assert the possession of this knowledge would be in the highest degree presumptuous. We can then never assert positively that any given substance is an element; we can only say that, the means at our command being insufficient to bring about the decomposition of a given

substance, we regard this substance as an element until such time shall arrive when, new means being given, it shall be shown to be a compound. Numerous instances of the change of opinion concerning the elementary character of different substances might be adduced, prominent among which are the metals of the alkalies, the oxides of which were for a time regarded as elements; chlorine, which was regarded as a compound body until it was shown that it cannot be decomposed, etc. etc. Thus the number of elements, as stated at any given time, is entirely dependent upon the state of chemical analysis at that time, and is never an expression of an absolute fact. At present, the number of elements known is 69. In other words, 69 distinct kinds of matter can be recognized.

The atoms that make up an elementary substance must necessarily be of the same kind. Accepting, then, the existence of atoms, an element may be defined as a substance made up of atoms of the same kind; and we shall see that the definition of an atom, that will be given further on, makes this definition of an element a strict one in every respect.

Compounds.—Observation shows us the existence of at least two varieties of compound substances. To only one of these, however, is the name *compound* strictly applicable, and then the name signifies a *chemical compound.* To the other class various names are applied, according to the nature of the substance, such for instance as *mechanical mixture, solution, alloy,* etc. Between mechanical mixtures and true chemical compounds there are generally such differences that they can be distinguished with comparative ease.

1. One of the most prominent characteristics of chemical compounds is the possession of properties which differ entirely from those of their constituents. Hydrogen, an inflammable gas, and oxygen, a gas and energetic supporter of combustion, combine to form a liquid, water, which is not inflammable and does not support combustion. Hydrochloric acid, a gas that turns vegetable blues red, and ammonia, a gas that turns vegetable reds blue, unite to form sal-ammoniac—a solid that is without influence upon vegetable colors. Chlorine, a gas, and mercury, a liquid, give a solid with none of the characteristic proper-

ties of either. The number of these examples might be *increased indefinitely, and in each case* a similar result would be reached.

2. Generally the constituents of a chemical compound cannot be separated from each other by mechanical means; but one of the so-called physical forces, as heat, light, electricity, or chemical affinity, is necessary.

3. The constituents of a compound are combined in fixed proportions by weight. If these constituents be brought together without reference to their quantities, and the proper condition be brought about to cause combination, a definite quantity of one combines with a definite quantity of the other; and, if the quantity of either present is in excess of the fixed quantity necessary for the formation of the compound, this excess will remain uncombined after combination has taken place. The proportions can be varied only to a very limited extent, and then not gradually, but according to a fixed rule. This is the fact that above all others enables us to assert positively that a given substance is or is not a chemical compound.

Mechanical Mixtures.—If oxygen and nitrogen be brought together, a homogeneous mixture of the two is formed, and this possesses the properties of both oxygen and nitrogen; such a mixture, for instance, is the atmosphere of the earth Many solids may be mixed in various ways, but no matter how finely they may be divided, nor how intimately they may be mixed, provided chemical combination does not take place, the constituents of the mixture can be separated by mechanical means, and the mixture possesses all the original properties of its constituents. In both these cases, further, the most varied quantities of the substances may be employed, and, under the same conditions, the mixtures will be formed just as readily with one proportion as with another.

Solutions and Alloys.—On the other hand, those compounds, which are known under the names of solutions and alloys, are more closely allied to chemical compounds. Gases, liquids, or solids may exist in the state of solution, that is, in combination with some liquid body, and to all appearance themselves in the liquid form. The external properties of one of the constituents are no longer recognizable, and they are, indeed, in part lost. A gas loses its

ordinary elasticity when dissolved in a liquid. A solid loses the cohesion which before held its particles together. Two liquids combined in this way lose some of their original properties. In all these instances the action between the particles of the dissolved substances and the particles of the solvents is greater in its effect than the cohesion that originally held together the particles of the solid or liquid, or the expansive force between the particles of the gas. Further, there are the alloys or compounds of two or more metals. These alloys present the appearance of perfectly homogeneous substances, but, nevertheless, possess most of the properties of the constituents. Here, too, the cohesion exerted between the particles of the original substances is modified when the substances are brought together.

A careful examination of the above-mentioned cases shows that there is generally a limit to the action. Substances that are soluble in water are not usually soluble to an unlimited extent; on the contrary, for any given temperature, the quantity of the substance that can be dissolved is fixed. But, between this fixed quantity and the smallest possible quantity of the substance, all proportions are equally well dissolved. Some liquids mix with each other in all proportions, a perfectly homogeneous liquid being the result. Others dissolve each other to only a limited extent, the limits being, as in the case of solids and liquids, fixed for any given temperature.

The subject of solution has recently received much attention, and some interesting laws have been discovered governing the conduct of dissolved substances. From what has been learned it appears most probable that between a dissolved substance and a solvent there is chemical action. The subject will be more fully treated further on.

It is plain, from the foregoing, that chemical compounds and elements are the only substances, the study of which can lead to definite conclusions concerning chemical action. Let us now return to that fundamental problem of chemistry—the determination of atomic weights. As it has been shown that results, reached by the methods already given, must necessarily be uncertain, we may now approach the subject from another side.

CHAPTER III.

EXAMINATION OF GASEOUS ELEMENTS AND COMPOUNDS.

THE methods of investigation applicable to substances differ according to the state of aggregation of the substances. Gases possess certain properties that solids and liquids do not possess, and solids and liquids have certain general properties that gases have not. The study of substances in the form of gas or vapor has led to most important results of lasting influence upon the science.

Investigations of Gay Lussac.—In the year 1808 Gay Lussac and Humboldt discovered the fact that when hydrogen and oxygen combine to form water, they combine in the proportion of 2 volumes of hydrogen to 1 volume of oxygen. The simplicity of this relation induced Gay Lussac to take up the study of other gaseous substances, with the object of determining whether similar relations exist between the volumes of other combining gases. His research enabled him soon after to deduce the following law of combination by volumes:—

> *When two or more gaseous substances combine to form a gaseous compound, the volumes* of the individual constituents as well as their sum bear a simple relation to the volume of the compound.*

Thus, when hydrogen and chlorine unite to form hydrochloric acid, it was found that 1 volume of hydrogen and 1 volume of chlorine form 2 volumes of hydrochloric acid gas. Two volumes of hydrogen and 1 volume of oxygen give 2 volumes of water-vapor; 2 volumes of nitrogen and 1 volume of oxygen give 2 volumes of nitrous oxide. Further, 3 volumes of hydrogen and 1 volume of nitrogen give 2 volumes of ammonia, etc.

* In all cases, where the volumes of gases are compared, the gases are, of course, supposed to be under the same conditions of pressure and temperature.

On comparing this result with that already obtained by Dalton, and making use of the atomic hypothesis, according to which combination between elements takes place between their atoms, it will be seen that a simple relation must exist between the volumes of gases and the relative number of atoms contained in these volumes. This we may express in general terms as follows:—

> *The number of atoms contained in a given volume of a gaseous substance bears a simple relation to the number of atoms contained in the same volume of other gaseous substances.*

But this plainly furnishes no foundation for the determination of atomic weights, inasmuch as we have no means of fixing the value of the "simple ratio," and without this we cannot determine the relative number of atoms contained in a given volume of gas. We know that 2 volumes of hydrogen combine with 1 volume of oxygen, and we know that 2 parts, by weight, of hydrogen combine with 16 parts, by weight, of oxygen. Further, according to the atomic hypothesis, a certain number of atoms of hydrogen of fixed weight combine with a certain number of atoms of oxygen of fixed weight, and these numbers bear a simple relation to each other; hence, the relation between the number of atoms of hydrogen in the 2 volumes and the number of atoms of oxygen in the 1 volume must be a simple one, but the facts do not furnish us with the data necessary to enable us to state what this relation is; without further aid, either from new facts or speculations, we cannot say what the atomic weights of these elements are.

Avogadro's Views.—The numbers expressing the specific gravities of gases or vapors are those numbers that express the relative weights of equal volumes of these gases or vapors. Hence, it is but restating, in another form, the law above laid down, to say that the specific gravities of gaseous bodies bear a simple relation to the atomic weights of these bodies. The force of this statement will readily be recognized on comparing the specific gravities of some elementary gases with the atomic weights of the same elements determined by chemical means. The atomic weights, as determined by chemical means, however, differed from each other according to

the method employed in this determination ; but the difference being that between one number and some multiple of that number, it is immaterial which of these numbers we employ for the purpose of the comparison. Let us, then, take the first of those determined. The following table hardly needs explanation. The numbers in the second column (d) represent the specific gravities of the elements in the form of gas or vapor ; the fourth column contains the ratios between the atomic weights (A) and $d = \frac{A}{d}$.

Element.	d.	A.	$\frac{A}{d}$.
Hydrogen	0.0692	1	14.45
Chlorine	2.440	35.4	14.51
Bromine	5.54	79.9	14.42
Iodine	8.716	126.5	14.51
Oxygen	1.10563	8	7.24
Sulphur	2.23	16	7.17
Selenium	5.68	39.4	6.94
Tellurium	9.08	62.5	6.88
Nitrogen	0.9713	14	14.41
Phosphorus	4.50	31	6.89
Arsenic	10.6	74.9	7.07
Mercury	7.03	99.9	14.21
Cadmium	3.94	55.9	14.19

From this it appears that the relation between the specific gravity and the atomic weight of seven of these thirteen elements is the same, being expressed by a number varying but little from 14.4. In the case of the six remaining elements of the list the relation is, also, virtually the same, about 7.1. And, in the latter case, the ratio is expressed by a number half as great as the first.

A consideration of these relations led Avogadro,* in 1811, to propose an hypothesis, which, if it is well founded, must prove of the greatest service in simplifying the problem of determining the atomic weights—at least of those elements of which gaseous compounds are known. It will be seen that, if in the above schedule the atomic

* In 1814 Ampère proposed a similar hypothesis.

weights of oxygen, sulphur, selenium, tellurium, phosphorus, and arsenic be doubled, the ratio $\frac{A}{d}$ for all the elements in the list will be the same constant number, viz., about 14.4. But the atomic weights above given have been determined purely empirically, and we are as much justified in considering the larger numbers as the true atomic weights as we are in accepting the ones given. If this change be made, then, for the above thirteen elements, the following statement will be true: The atomic weights are to each other as the specific gravities of the vapors. An examination of compound gaseous substances showed further that a simple relation also exists between their specific gravities and the numbers expressing the sum of the atomic weights of the constituents, these sums being to each other as the specific gravities. Avogadro's hypothesis to account for these relations may be stated in the following words:—

> *All gases and vapors, without exception, contain, in the same volume, the same number of ultimate particles or molecules.*

The molecules were not considered to be identical with the atoms, and it is well here to draw the distinction between the two as clearly as possible. Molecules of compounds, as understood by Avogadro, and as understood at present, are the hypothetical smallest particles of these compounds. The molecule of water is the smallest particle of water that can exist as water. As water, however, is composed of two elements, of course, the smallest particle of water must necessarily still be divisible into these constituents. The component parts of molecules are called atoms, and these are indivisible. In the case of water, the molecule has the same composition as the mass of the compound, but, as will be shown, this molecule of water consists of two atoms of hydrogen and one atom of oxygen. The holding together of the two atoms is a chemical act. That which holds the molecule together is called cohesion.

Now, there are good reasons, which will be considered below, for believing that, in their internal structure, elementary substances are, in some respects, analogous to compounds, and this belief was made a fundamental con-

dition of Avogadro's hypothesis. According to this, it is, in most cases, impossible, by purely mechanical means, to subdivide an element so far as to reach its atoms; but, if we suppose it divided as far as possible by such means, we reach, as in the case of compounds, the molecule of the element, which is the smallest particle of the element that can exist and play the part of the element. This molecule, however, usually consists of atoms, that are held together by a chemical act, and can hence be separated only by means other than mechanical.

From these considerations definitions of the terms *atom* and *molecule* follow :—

A molecule is the smallest particle of a compound or element that is capable of existing in a free state. A breaking up of the molecule necessitates the destruction of the characteristic properties of the compound, and almost always of those of the element.

Atoms are the indivisible constituents of molecules. They are the smallest particles of elements that take part in chemical reactions, and are, for the greater part, incapable of existence in the free state, being generally found in combination with other atoms, either of the same kind or of different kinds.

And now the justice of the definitions of elements and compounds given above will be recognized, viz., an element is a substance made up of atoms of the same kind; a compound is a substance made up of atoms of different kinds.

Recognizing thus fully the distinction between atoms and molecules, we are prepared to follow further the reasoning of Avogadro.

The experiments of Gay Lussac had already proved that, under the influence of heat, all gases expand in the same proportion for the same increase of temperature, and diminish in volume to the same extent for the same decrease of temperature. Further, Mariotte and Boyle had shown that all gases conduct themselves in the same way under the influence of increased or decreased pressure; that for the same increase or decrease of pressure the resulting decrease or increase of volume is the same for the same volume of all gases. These facts considered independently would lead to the suspicion that all gases possess a similar internal structure, and the simplest hypothesis to account for this is the hypothesis of Avogadro—that the same volumes of all gaseous bodies contain the

same number of molecules. This subject has been treated exhaustively from a purely physical point of view. The mechanical theory of gases being accepted, it has been shown that the hypothesis of Avogadro follows as a necessary consequence; and then, by a purely mathematical process of reasoning, it has been shown that the hypothesis is an absolute necessity. A discussion of the subject in the direction indicated cannot be taken up here.

As a grand result of the investigations that have been made on the internal structure of gases, it may be stated that Avogadro's hypothesis has throughout asserted its correctness, and it has long been recognized as of fundamental importance in the science of chemistry. It is at present almost universally accepted by chemists, and is generally referred to as a *law*.

Determination of Molecular Weights.—What, then, do we gain by accepting the hypothesis? It is plain that if equal volumes of all gases contain the same number of molecules we have a means given us at once for ascertaining the relative weights of these molecules. We have merely to determine the relative weights of equal volumes of the gases, and the numbers obtained will bear the same relations to each other as the molecular weights. Then accepting the weight of some molecule as a standard, and expressing the weights of the others in terms of this standard, the molecular weights are determined. Let us, for example, take hydrochloric acid as the standard molecule. As this compound contains 35.4 parts by weight of chlorine to 1 of hydrogen, the smallest figure which we can take to represent its molecular weight, without representing the weight of hydrogen by a figure less than 1, is 36.4. By further study of hydrochloric acid it is found that no facts are known that require us to select a figure larger than 36.4 for its molecular weight. We accordingly accept this as the molecular weight of hydrochloric acid. We now determine the specific gravity of the gas, and express the result in terms of air. The figure is 1.247, or, to be explicit, if the weight of a given volume of air be represented by 1, then the weight of the same volume of hydrochloric acid gas is represented by 1.247. As, according to Avogadro's hypothesis, the molecular weights of gaseous bodies bear the same relation to each other as their specific gravities, it is only necessary to determine in

one particular case what relation exists between the molecular weight and the specific gravity. The molecular weight accepted for hydrochloric acid, for the reasons above given, is 36.4; the specific gravity, determined by actually weighing the gas, is 1.274. The relation between the two figures is expressed thus, $\frac{36.4}{1.274} = 28.57$; or, calling the specific gravity d, and the molecular weight M, we have for hydrochloric acid $\frac{M}{d} = 28.57$, $M = d \times 28.57$. Having determined the relation between the specific gravity and the molecular weight of one gaseous substance, we have, however, determined it for all, and we thus have in our possession a method for determining molecular weights that depend upon the determination of the specific gravities of gases or vapors. If the rule is perfect, and the figures obtained by experiment were absolutely accurate, then, by dividing the molecular weight of any gaseous substance by its specific gravity, we should in every case obtain the same quotient. Owing partly to the imperfection of the methods for determining specific gravities and for analyzing chemical compounds, the figures actually obtained do not give exactly the quotient obtained in the case of hydrochloric acid. The average of the results is more nearly 28.88, and as this is the figure obtained by dividing the molecular weight of hydrogen by the specific gravity, it is the one commonly given in stating the rule. Instead of being $M = d \times 28.57$, it is $M = d \times 28.88$.

Applying the rule to the determination of molecular weights, we obtain results which approximate the truth, and which enable us to decide whether the molecular weight is a certain figure or a multiple of this figure. Chemical analysis then comes to our aid and tells us exactly what the number is. To illustrate this, take the case of water. We find by determining the specific gravity of water vapor and multiplying by 28.88 that the molecular weight is 17.99. This enables us at once to decide between the various possibilities, 9, 18, 27, etc. If we now determine with great accuracy the proportions by weight in which hydrogen and oxygen are combined with each other in water, we shall be able to state exactly what the molecular weight of water is. According to the most reliable investigations the figure is 17.96. The coincidence

of the numbers determined by the two methods in the case of a few elements and compounds will be seen on examining the subjoined table. The numbers under *M* are those found by the analytical method, that one of a series of multiples being selected which agrees most nearly with the number found according to the rule $M = 28.88 \times d$.

Name.	Specific gr. = *d*.	$28.88 \times d$.	*M*.
Hydrogen	0.06926	2	2
Nitrogen	0.9713	28.05	28
Oxygen	1.10563	31.93	31.9
Sulphur	2.23	64.4	63.9
Chlorine	2.45	70.75	70.8
Cadmium	3.94	113.78	111.7
Phosphorus	4.35	125.62	123.8
Bromine	5.54	159.99	159.5
Selenium	5.68	164.03	157.74
Mercury	6.98	201.58	199.8
Water	0.623	17.99	17.96
Hydrochloric acid	1.247	36.11	36.4
Sulphur dioxide	2.247	64.89	63.9
Ammonia	0.597	17.24	17
Phosphorus trichloride	4.88	140.93	137.1
Arsenic trichloride	6.30	181.94	181
Boron chloride	3.942	113.84	117
Marsh-gas	0.557	16.08	16
Methyl chloride	1.736	50.13	50.7
Chloroform	4.20	121.29	119.1
Tin chloride	9.20	265.69	258.9
Silicon chloride	5.94	171.55	169.5
Zinc-methyl	3.29	95.02	94.8
Aluminium chloride	9.35	270.03	266.3
Ferric chloride	11.39	328.94	324

Number of Atoms in the Molecules of Elements.—Although we are thus enabled to determine by a simple process the molecular weights of those elements which are gases under ordinary conditions, or which can be converted into gases, an important part of the problem—the determination of the atomic weights—yet remains to be solved. If we knew in each case how many atoms are contained in a molecule, our difficulties would be at an end; but this we plainly do not know without the introduction of considerations of a different kind from those

with which we have had to deal thus far. Taking hydrochloric acid as the standard in determining the molecular weights, and representing its molecular weight by 36.4, because that is the smallest figure permissible, if the hydrogen in it is not to be expressed by a figure less than 1, we find that the molecular weight of hydrogen, determined by the rule of Avogadro, is 2. Now the part of hydrogen contained in hydrochloric acid, which is represented by 1, must be at least an atom of hydrogen. Or, further, the 36.4 parts of hydrochloric acid, representing the molecule, must be made up of at least one atom of hydrogen, weighing 1 part, and one atom of chlorine, weighing 35.4 parts. But, as we find that the molecule of hydrogen weighs 2 parts, it follows that the molecule must be at least twice as heavy as the atom, or the molecule must contain at least two atoms. We may also reason as follows, with reference to some of the simpler chemical compounds: Given hydrochloric acid, it is required to know how many atoms are contained in a molecule of hydrogen and in a molecule of chlorine. If in a certain volume of hydrogen there are contained say 100 molecules, then in the same volume of chlorine there are contained the same number of molecules. Now it is known that 1 volume of hydrogen combines with 1 volume of chlorine. Two volumes of hydrochloric acid gas are formed, and, according to the hypothesis, these two volumes in the case under consideration contain 200 molecules But each molecule of hydrochloric acid must contain at least one atom of chlorine and one atom of hydrogen; hence, in 100 molecules of hydrogen and 100 molecules of chlorine there must be at least 200 atoms of chlorine and 200 atoms of hydrogen, or a molecule of either hydrogen or chlorine must contain at least two atoms. Further, as no simpler compound of hydrogen or of chlorine is known than hydrochloric acid, any conclusions which we may draw from a consideration of this compound must be valid for all compounds of these elements. The supposition that two atoms form the molecule of hydrogen and of chlorine satisfies all the facts known to us, and we hence rest with this supposition. It must, however, be distinctly borne in mind that no proof is here given of the absolute number of atoms contained in the molecules of hydrogen and chlorine. We can only say that *at least* 2 atoms must be present in each of the

molecules. There may be a much greater number, but the data permit no conclusion beyond this number 2.

For all similar cases a similar process of reasoning may be employed, and with the same results. Whenever 1 volume of an elementary gas or vapor combines with 1 volume of another elementary gas or vapor to form 2 volumes of a compound gas or vapor, we are justified in concluding that each molecule of these elements contains two atoms. The elements that come under this head are hydrogen and chlorine.

If we pass to oxygen, we find a material difference in the conduct: 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of water-vapor. Let us reason as above. If in 1 volume of oxygen there are contained 100 molecules, then in 2 volumes of hydrogen there are 200 molecules. These 300 molecules combine to form 200 molecules of the compound. Now, in the molecule of water, there must be contained at least 1 atom of oxygen and 1 atom of hydrogen; hence, there must be at least 200 atoms of oxygen and 200 atoms of hydrogen. But we know that in the original 200 molecules of hydrogen there were contained 400 atoms; hence, in each molecule of water there must be 2 atoms of hydrogen. Water is the simplest compound of oxygen known to us (*i. e.*, it contains the smallest quantity of oxygen in the molecule), and on this account we suppose the molecule of water to contain 1 atom of oxygen. If, then, each molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen, in the 200 molecules of water there are 200 atoms of oxygen and 400 atoms of hydrogen, and these are obtained from 100 molecules of oxygen and 200 molecules of hydrogen. Therefore, each molecule of oxygen, as well as each molecule of hydrogen, contains 2 atoms.

Another method of reasoning, starting from entirely different facts, also led Favre and Silbermann to suggest that the molecule of oxygen consists of 2 atoms. They proved that carbon, when burned in nitrous oxide, evolves more heat than when burned in oxygen. The simplest interpretation of this fact is that, in each experiment, a chemical combination is destroyed while another is formed; and that the amount of heat actually evolved is the difference between the amount of heat disengaged by the union of carbon with oxygen and the amount of heat absorbed by the decomposition of the oxide of oxygen in the first

instance, and of oxide of nitrogen in the second. And, if the thermic effect is less with oxygen than with nitrous oxide, that is due to the circumstance that more heat is absorbed in the decomposition of the oxide of oxygen (the molecule of oxygen O_2) than in the decomposition of the molecule of nitrous oxide.

One volume of nitrogen combines with 3 volumes of hydrogen to form 2 volumes of ammonia. Hence, in the molecule of ammonia there are 3 atoms of hydrogen, and ammonia being the simplest compound of nitrogen, we suppose that these 3 atoms of hydrogen are combined with 1 atom of nitrogen. As each molecule of ammonia contains 1 atom of nitrogen, and as, further, there are formed twice as many molecules of ammonia as there were molecules of nitrogen originally, it follows that the molecule of nitrogen contains at least 2 atoms.

By this means we are enabled to determine the atomic weight of the elements mentioned, for if in their molecules 2 atoms are contained, we have only to divide the molecular weight—found by Avogadro's rule, and corrected by analytical methods—by two. But accepting the atomic weights of hydrogen, chlorine, bromine, and iodine as known, we are enabled by another process to determine the atomic weights of such elements as combine with these to form gaseous compounds.

Take, again, water. We find by a comparison of the compounds of oxygen that the molecule of water, as stated above, contains as small a quantity of this element as any other compound; and hence we suppose this quantity to represent 1 atom. We first find the molecular weight from the specific gravity of the vapor. This is 18. We analyze the compound, and find that it contains 88.89 per cent. oxygen, and 11.11 per cent. hydrogen, or 8 parts of oxygen to 1 part of hydrogen. Therefore in 18 parts by weight, which represent the molecule, there are contained 16 parts of oxygen and 2 parts of hydrogen. The atomic weight of oxygen is hence 16, and in water 1 atom of oxygen is combined with 2 atoms of hydrogen. In the same way, on comparing the molecular weights of the compounds of nitrogen we find that the relative quantity of this element contained in the molecule of ammonia is as small as in any other. The molecular weight of ammonia we find to be 17. The analysis shows that the elements are combined in the proportion of 14 parts by

weight of nitrogen to 3 parts by weight of hydrogen. Hence 14 is the atomic weight of nitrogen, and the molecule of ammonia contains 1 atom of nitrogen and 3 atoms of hydrogen.

Molecules of Elements which contain more or less than two Atoms.—The molecules of the elements considered contain each at least 2 atoms. This, however, is not true of the molecules of all elements.

Among those compounds of phosphorus which may be looked upon as containing 1 atom of this element in the molecule is phosphine. The molecular weight of phosphine is 34. The elements are contained in it in the proportion of 31 parts of phosphorus to 3 parts of hydrogen. Hence 31 is the atomic weight of phosphorus. On the other hand, we find the molecular weight of phosphorus itself to be 124, which shows that at least 4 atoms are contained in the molecule. The same is true of arsenic.

For reasons similar to those given above the molecule of mercuric chloride is supposed to contain one atom of mercury. The molecular weight of this compound is found to be 270.5, and the elements are contained in it in the proportion of 199.8 parts of mercury to 70.7 parts of chlorine, which gives 199.8 as the atomic weight of mercury, and the atom of this element is combined with two atoms of chlorine. The molecular weight of mercury is 200; hence, in the molecule of mercury there is contained but one atom. The same coincidence of atomic and molecular weight is noticed in the case of cadmium and zinc.

Kundt and Warburg have described an interesting experiment, the results of which also show that the molecule of mercury in all probability consists of a single atom. The quantity of heat contained in a gas is defined as the total energy of its molecules, and this energy consists solely in progressive motion, if the molecule is looked upon as a mere material point. According to this it is a simple matter to calculate the relation between the specific heat of a gas at constant volume and the specific heat at constant pressure. It has been found that in the case of the gases examined, the theoretical value of this ratio is larger than the value actully observed. If c represents the specific heat at constant volume, and c' the specific heat at constant pressure, then $\frac{c'}{c} = k$ represents the ratio

above referred to. According to the theory, $k = 1.67$, whereas observation gives $k = 1.405$. In other words, it requires more heat to raise the temperature of a gas, the volume remaining unchanged, than the theory demands. The heat that thus disappears may be transformed into an inter-molecular motion, *i. e.*, the atoms, composing the molecule, may have a motion relative to some centre of gravity. This motion would not show itself as temperature. If the molecule of the gas consists of one atom, then the theoretical and observed value of k should be identical. The examination of mercury gave for k the value 1.67, which is that above given as the result of calculation. It is thus shown by a method entirely independent of chemistry, that the molecule of mercury conducts itself like a material point, and this could only be the case if it consisted of one atom.

Varying number of Atoms in the Molecule of one and the same Element.—The specific gravity of the vapor of sulphur was stated in the above table (p. 41) to be 2.23, and this leads to the molecular weight 63.9. Now, it has been found that the specific gravity of sulphur vapor varies according to the temperature at which it is determined. The determinations, which gave the number 2.23, were made at temperatures above 800° C. (860° and 1040°). Other determinations, however, made below 800° gave different results. At 524° (Dumas) and 508° (Mitscherlich) the specific gravity was found to be 6.62 and 6.90 respectively, or three times as great as at the higher temperatures. These latter determinations gave the molecular weight approximately 192, and, if 32 be the atomic weight of sulphur, then in the molecule of the vapor below 800° there are contained 6 atoms, whereas above 800° there are contained only 2 atoms in the molecule. According to recent researches by Biltz, the specific gravity of the vapor of sulphur changes gradually up to 800°, and there is no evidence of the existence of the molecules S_6, S_4. At 800° the value found points to the formula S_2, and there is then no change through an interval of over 900°, as has been shown by V. Meyer and Biltz. On the other hand, Ramsay holds that the results of Biltz do not prove the non-existence of the molecules, S_6 and S_4, but rather that these and even more complex molecules such as S_{10}, exist. Selenium, so similar to sulphur in all other respects, presents similar phenomena, though not in so marked a

degree. Here, too, it is noticed that the specific gravity of the vapor decreases with an increase of temperature.

Analogous results have been obtained in the case of iodine. The normal specific gravity of iodine vapor is 8.8, corresponding to the molecular weight, 254. It was first shown by Victor Meyer that at 1027° C. the specific gravity is reduced to 5.8. J. M. Crafts and F. Meier showed that at 1468° it is still further reduced, becoming 5.1. Victor Meyer then succeeded in reducing it to 4.5 by heating to a higher temperature; and, finally, Crafts and Meier proved that by a further elevation of temperature the specific gravity is not reduced below the value 4.5, which is very nearly half the normal. The simplest interpretation of these facts is this: Under ordinary conditions the molecule of the vapor of iodine consists of 2 atoms. When the temperature is raised there is a gradual decomposition of the molecules into 2 atoms each. This decomposition continues, as the temperature becomes higher, until finally all the molecules are broken up into atoms. When this limit is reached, no further decomposition being possible, the specific gravity remains unchanged, even though the temperature be raised still higher. The fact that the reduction in the specific gravity stops when it reaches half the normal is especially significant, as it furnishes strong evidence of the presence of 2, and only 2, atoms, in the molecule of iodine.

The application of the above method to the determination of the molecular weights of elements is limited, as *only a few* of these elements can be converted into vapor. Of many elements, however, compounds are known that are capable of conversion into vapor, or are themselves gaseous, and, as the molecular weights of these compounds can be determined, the atomic weights of the elements of which they are made up can also be determined. The following table contains a number of such compounds, together with the specific gravities (d); the products of the specific gravities by the constant 28.88 ($d \times 28.88$); the molecular weights as found by analytical methods (M); and, finally, the relative quantities of the constituents of the compounds contained in the molecules as determined by analysis:—

Name.	*d.*	*d* × 28.88	*M.*	Constituents.
Aluminic chloride .	9.35	270	266.3	54.08 parts aluminium.
				212.22 " chlorine.
Aluminic bromide .	18.6	537.2	532.64	54.08 " aluminium.
				478.56 " bromine.
Aluminic iodide . .	27	780	813.32	54.08 " aluminium.
				759.24 " iodine.
Antimony trichloride	7.8	225.3	225.71	119.6 " antimony.
				106.11 " chlorine.
Triethylstibine . .	7.44	214.8	206.42	119.6 " antimony.
				71.82 " carbon.
				15 " hydrogen.
Antimony trioxide .	19.79	571.5	574.16	478.4 " antimony.
				95.76 " oxygen.
Arsenic triiodide . .	16.1	464.9	454.52	74.9 " arsenic.
				379.62 " iodine.
Arsine	2.7	77.97	77.9	74.9 " arsenic.
				3 " hydrogen.
Arsenic trichloride .	6.3	181.9	181.01	74.9 " arsenic.
				106.11 " chlorine.
Arsenic trioxide . .	13.79	398.3	396.36	299.6 " arsenic.
				95.76 " oxygen.
Cacodyl chloride . .	4.56	131.7	140.21	74.9 " arsenic.
				23.94 " carbon.
				6 " hydrogen.
				35.37 " chlorine.
Cacodyl cyanide . .	4.65	134.3	130.82	74.9 " arsenic.
				35.91 " carbon.
				14.01 " nitrogen.
				6 " hydrogen.
Bismuth trichloride .	11.35	327.8	313.41	207.3 " bismuth.
				106.11 " chlorine.
Boric chloride . .	3.942	113.8	117.01	10.9 " boron.
				106.11 " chlorine.
Boric fluoride . . .	2.312	66.8	68.08	10.9 " boron.
				57.18 " fluorine.
Boric bromide . .	8.78	253.5	250.18	10.9 " boron.
				239.28 " bromine.
Trimethylborine . .	1.93	55.7	55.81	10.9 " boron.
				35.91 " carbon.
				9 " hydrogen.
Cadmium bromide .	9.25	267.1	271.22	111.7 " cadmium.
				159.52 " bromine.
Marsh-gas	0.557	16.1	15.97	11.97 " carbon.
				4 " hydrogen.
Methyl fluoride . .	1.186	34.3	34.03	11.97 " carbon.
				3 " hydrogen.
				19.06 " fluorine.

Name.	d.	d × 28.88	M.	Constituents.
Methyl chloride . .	1.731	50	50.34	11.97 parts carbon. 3 “ hydrogen. 35.37 “ chlorine.
Methyl bromide . .	3.253	93.9	94.73	11.97 “ carbon. 3 “ hydrogen. 79.76 “ bromine.
Methyl iodide . .	4.883	141	141.51	11.97 “ carbon. 3 “ hydrogen. 126.54 “ iodine.
Methyl nitrate . .	2.64	76.2	76.86	11.97 “ carbon. 3 “ hydrogen. 14.01 “ nitrogen. 47.88 “ oxygen.
Methyl alcohol . .	1.12	32.3	31.93	11.97 “ carbon. 4 “ hydrogen. 15.96 “ oxygen.
Carbon monoxide .	0.968	27.96	27.93	11.97 “ carbon. 15.96 “ oxygen.
Carbon dioxide . .	1.529	44.16	43.89	11.97 “ carbon. 31.92 “ oxygen.
Chloroform . . .	4.2	121.3	121.08	11.97 “ carbon. 3 “ hydrogen. 106.11 “ chlorine.
Carbon tetrachloride	5.24	151.3	153.45	11.97 “ carbon. 141.48 “ chlorine.
Carbon oxichloride	3.505	101.2	98.67	11.97 “ carbon. 15.96 “ oxygen. 70.74 “ chlorine.
Carbon oxisulphide	2.105	60.8	59.91	11.97 “ carbon. 15.96 “ oxygen. 31.98 “ sulphur.
Carbon sulphide . .	2.645	76.39	75.93	11.97 “ carbon. 63.96 “ sulphur.
Hydrocyanic acid .	0.948	27.4	26.98	1 part hydrogen. 11.97 parts carbon. 14.01 “ nitrogen.
Cyanogen chloride .	2.13	61.5	61.35	11.97 “ carbon. 14.01 “ nitrogen. 35.37 “ chlorine.
Cyanic acid . . .	1.5	43.3	42.94	11.97 “ carbon. 14.01 “ nitrogen. 15.96 “ oxygen. 1 part hydrogen.
Hydrochloric acid .	1.247	36	36.37	35.37 parts chlorine. 1 part hydrogen.
Chromic oxychloride	5.55	160.3	155.11	52.45 parts chromium. 31.92 “ oxygen. 70.74 “ chlorine.

Name.	*d*.	*d* × 28.88	*M*.	Constituents.
Cuprous chloride .	6.93	200.1	197.10	126.36 parts copper. 70.74 " chlorine.
Indium chloride . .	7.87	227.3	219.51	113.4 " indium. 106.11 " chlorine.
Hydriodic acid . .	4.443	128.3	127.54	126.54 " iodine. 1 part hydrogen.
Ferric chloride . .	11.07	320	323.98	111.76 parts iron. 212.22 " chlorine.
Lead chloride . . .	9.5	274.4	277.14	206.4 " lead. 70.74 " chlorine.
Lead methyl . . .	9.6	277.2	266.28	206.4 " lead. 47.88 " carbon. 12 " hydrogen.
Mercuric chloride .	9.8	283	270.54	199.8 " mercury. 70.74 " chlorine.
Mercuric bromide .	12.16	351.2	359.32	199.8 " mercury. 159.52 " bromine.
Mercuric iodide . .	16.2	468	452.88	199.8 " mercury. 253.08 " iodine.
Mercury methyl . .	8.29	239.4	229.74	199.8 " mercury. 23.94 " carbon. 6 " hydrogen.
Mercury ethyl . .	9.97	287.9	367.68	199.8 " mercury. 47.88 " carbon. 10 " hydrogen.
Molybdic chloride .	9.46	273	272.75	95.9 " molybdenum 176.85 " chlorine.
Niobic chloride . .	9.6	277.2	270.55	93.7 " niobium. 176.85 " chlorine.
Niobic oxychloride .	7.88	227.6	215.77	93.7 " niobium. 15.96 " oxygen. 106.11 " chlorine.
Ammonia	0.597	17.2	17.01	14.01 " nitrogen. 3 " hydrogen.
Nitric oxide . . .	1.039	30	29.97	14.01 " nitrogen. 15.96 " oxygen.
Nitrous oxide . . .	1.520	43.9	43.98	28.02 " nitrogen. 15.96 " oxygen.
Osmium tetroxide .	8.89	256.7	258.84	195 " osmium. 63.84 " oxygen.
Water	0.623	17.99	17.96	15.97 " oxygen. 2 " hydrogen.
Phosphine	1.18	34.1	33.96	30.96 " phosphorus. 3 " hydrogen.
Phosphorus trichloride	4.85	140	137.07	30.96 " phosphorus. 106.11 " chlorine.

Name.	d.	d × 28.88	M.	Constituents.
Phosphorus oxichloride	5.40	155.9	153.03	30.96 parts phosphorus.
				15.96 " oxygen.
				106.11 " chlorine.
Phosphorus sulphochloride	5.88	169.8	169.05	30.96 " phosphorus.
				31.98 " sulphur.
				106.11 " chlorine.
Triethylphosphine oxide	4.60	132.8	133.74	30.96 " phosphorus.
				15.96 " oxygen.
				71.82 " carbon.
				15 " hydrogen.
Phosphorus pentasulphide	7.65	220.9	221.82	61.92 " phosphorus.
				159.90 " sulphur.
Selenium dioxide	4.03	116.4	110.79	78.87 " selenium.
				31.92 " oxygen.
Silicic chloride	5.94	171.5	169.48	28 " silicon.
				141.48 " chlorine.
Silicic fluoride	3.6	104	104.24	28 " silicon.
				76.24 " fluorine.
Silicic iodide	19.1	551.6	534.14	28 " silicon.
				506.14 " iodine.
Silicon ethyl	5.14	148.4	143.76	28 " silicon.
				95.76 " carbon.
				20 " hydrogen.
Sulphur dioxide	2.247	64.9	63.9	31.98 " sulphur.
				31.92 " oxygen.
Sulphur trioxide	3.01	86.9	79.76	31.98 " sulphur.
				47.88 " oxygen.
Sulphuryl chloride	4.67	134.8	134.64	31.98 " sulphur.
				31.92 " oxygen.
				70.74 " chlorine.
Hydrogen sulphide	1.191	34.4	33.98	31.98 " sulphur.
				2 " hydrogen.
Tantalic chloride	12.9	372.5	358.85	182 " tantalum.
				176.85 " chlorine.
Thallic chloride	8.15	235.4	239.07	203.7 " thallium.
				35.37 " chlorine.
Stannous chloride	12.96	374.3	375.28	234.8 " tin.
				141.48 " chlorine.
Stannic chloride	9.20	265.7	258.88	117.4 " tin.
				141.48 " chlorine.
Tin ethyl	8.02	231.6	233.16	117.4 " tin.
				95.76 " carbon.
				20 " hydrogen.

Name.	d.	$d \times 28.88$	M.	Constituents.
Tin triethyl chloride	8.43	243.4	239.59	117.4 parts tin.
				35.37 " chlorine.
				71.82 " carbon.
				15 " hydrogen.
Tin triethyl bromide	9.92	286.5	283.98	117.4 " tin.
				79.76 " bromine.
				71.82 " carbon.
				15 " hydrogen.
Titanic chloride . .	6.84	197.5	189.48	48 " titanium.
				141.48 " chlorine.
Tungsten pentachloride	12.7	366.7	360.45	183.6 " tungsten.
				176.85 " chlorine.
Tungsten hexachloride	13.2	381.2	395.82	183.6 " tungsten.
				212.22 " chlorine.
Tungsten oxichloride	11.84	342	341.04	183.6 " tungsten.
				15.96 " oxygen.
				141.48 " chlorine.
Uranium chloride .	13.3	384.1	381.28	239.8 " uranium.
				141.48 " chlorine.
Uranium bromide .	19.46	562	558.84	239.8 " uranium.
				319.04 " bromine.
Vanadium tetrachloride	6.78	195.8	192.58	51.1 " vanadium.
				141.48 " chlorine.
Vanadium acichloride	6.11	176	173.17	51.1 " vanadium.
				15.96 " oxygen.
				106.11 " chlorine.
Zinc chloride . . .	4.57	132	135.62	64.88 " zinc.
				70.74 " chlorine.
Zinc methyl . . .	3.29	95.1	94.82	64.88 " zinc.
				23.94 " carbon.
				6 " hydrogen.
Zinc ethyl	4.62	133	122.76	64.88 " zinc.
				47.88 " carbon.
				10 " hydrogen.
Zinc amyl	6.95	200.7	206.58	64.88 " zinc.
				119.70 " carbon.
				22 " hydrogen.
Zirconium chloride .	8.15	235.4	232.42	90.94 " zirconium.
				141.48 " chlorine.

This list contains compounds of thirty elements, and, by means of these compounds, supposing that they contain at least one of their elements in the smallest possible

proportion, we can determine the atomic weights of the elements concerned. It will be seen, however, that while the hypothesis of Avogadro furnishes a method which enables us to state positively what the molecular weight of any gaseous compound is, it does not furnish a means for the determination of atomic weights directly. After examining the various compounds of an element, that one is selected which contains the smallest quantity of the element in the molecule, and then, without further proof, we say this smallest quantity represents the atom. Thus it is evident that the atomic weights, as determined by this method, rest upon a more or less doubtful basis. For practical purposes, however, this is not a serious matter; inasmuch as, although we cannot assert that the weight found really represents the atomic weight, we can assert that it represents the weight of that portion of the element which conducts itself as an atom, *i. e.*, throughout the series of changes which it undergoes in its compounds it is indivisible.

Other Proofs of the Fact that the Molecules of Elements contain more than one Atom.—It has been stated above that the molecules of elements contain, in most cases, more than one atom; and it has been shown that, if the hypothesis of Avogadro be accepted, we are necessarily led to this conclusion by a simple consideration of the molecular weights of elements and their compounds. The question will naturally suggest itself: Is there any evidence independent of Avogadro's hypothesis, that the molecules of elements consist of more than one atom? There are at least some indications that this is the fact.

A number of the elements, as we ordinarily meet with them in the free state, conduct themselves as comparatively inactive substances. Take, for instance, hydrogen. In its usual condition, this element does not act readily upon most other elements and compounds. It can be brought in direct contact with most substances without effecting any change whatever in them. If, however, it be set free from one of its compounds, and, at the instant it is set free, it be allowed to act upon some other substance, it is found to be a comparatively active element, capable of effecting very material changes in other substances. The same is true of oxygen, nitrogen, and other elements.

They are much more active in the *status nascendi* than in the free state. How can this be explained? Most readily by supposing the molecules of these elements, in the free state, to contain more than one atom combined with each other. Now, if it be required that an element thus constituted shall combine with another substance, it is first necessary that the force which holds together the atoms be overcome; the atoms must be torn asunder before they can act as atoms; or, in other words, a decomposition must be effected before the required combination can take place.

Sometimes the attraction exerted by an atom of one element for an atom of another is so strong that this decomposition is effected, and the combination then takes place. Thus, if we bring hydrogen and chlorine together, both in the free state, they combine. In this case, the chlorine atom attracts the hydrogen atom more strongly than the hydrogen atom attracts its fellow, or the chlorine atom its own chlorine atom. On the other hand, numerous instances of the opposite kind might be adduced. One will suffice for the purpose of illustration. When hydrogen gas is passed through nitric acid no change takes place. But when zinc is dissolved in nitric acid, a portion of the acid is decomposed by the hydrogen evolved. The hydrogen atoms, set free from the nitric acid, find the acid present, and act upon it in preference to combining to form free hydrogen; the elements in combination with nitrogen are forcibly removed and the hydrogen takes their place, forming ammonia.

Ordinary oxygen contains two atoms in the molecule. Ozone, another variety of oxygen, has the density 1.658, from which its molecular weight is found to be nearly 48. Now as the atomic weight of oxygen, according to previous determinations, is 15.96, it follows that the molecule of ozone contains three atoms. The difference between the two forms of oxygen is thus explained. Ozone is comparatively unstable. It gives up its extra atom with great ease to substances with which it comes in contact, and causes thus energetic oxidation. When heated to 300°, it is decomposed, forming ordinary oxygen, and then an increase of volume is observed. In this case, if no foreign substance be present with which the liberated atom can unite, it unites with another atom of the same

kind. When it acts upon other substances, the original volume of the gas remains unchanged. It thus appears that the two atoms of the molecule of ordinary oxygen are held together more firmly than the three atoms in the molecule of ozone. Here again the different actions of the two varieties can apparently be best explained by supposing in each case the molecule to consist of more than one atom.

These and similar considerations serve to strengthen the conclusion to which we are led by accepting Avogadro's hypothesis, and hence, in turn, to increase the probability that the hypothesis is in fact a law.

Molecular Formulas of Gaseous Compounds.—When the atomic weights of the elements are once determined, the law of Avogadro, taken together with chemical analysis, is sufficient to enable us to determine the molecular formulas of gaseous chemical compounds,—a problem, the solution of which without this rule is in many cases exceedingly difficult, and, indeed, at times impossible. Let us suppose the atomic weights of carbon (11.97), hydrogen (1), and oxygen (15.96) to be known. We analyze a certain compound, and find that it contains 37.49 per cent. carbon, 12.53 per cent. hydrogen, and 49.98 per cent. oxygen. This gives the atomic proportion 1 of carbon, 4 of hydrogen, and 1 of oxygen; and hence the simplest formula that can be assigned to the compound is CH_4O. But the formulas $C_2H_8O_2$ or $C_3H_{12}O_4$, etc., also satisfy the results of the analysis. The molecular weight is next determined by Avogadro's method, and it is found to be approximately 32; and, as the sum of the weights of the atoms in a molecule of a compound of the formula CH_4O is 31.93, this formula is thus shown to be the correct one.

Apparent Exceptions.—All formulas of chemical compounds at present in use are intended to represent molecules of the compounds. They are molecular formulas. They represent those quantities of the compounds which, in a gaseous condition, would occupy the same space as a molecule of hydrogen. If we take two volumes of hydrogen as the standard of comparison, then the formulas of compounds represent two volumes of the same size. To this there are apparent exceptions. When ammonia acts upon hydrochloric acid, the two gases combine in the proportion

of 1 vol. of the one to 1 vol. of the other, forming a solid compound which contains 26.25 per cent. nitrogen, 7.49 per cent. hydrogen, and 66.36 per cent. chlorine. This gives the atomic proportion 1 nitrogen, 4 hydrogen, and 1 chlorine; and the simplest formula that can be assigned to the compound, provided the atomic weights of nitrogen, hydrogen, and chlorine are respectively 14.01, 1, and 35.37, is NH_4Cl. On now determining the molecular weight by Avogadro's method, this is found to be 26.69, or half that required by the above formula. Evidently, it is impossible for a molecule made up of chlorine, nitrogen, and hydrogen, with the atomic weights above assigned to them, to have as small a weight as 26.69; and, to satisfy the results of this determination, we should be obliged to write the formula $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$, and thus accept the existence of half atoms, which is absurd. We might also imagine the atomic weight of nitrogen and chlorine, as already determined, to be just twice too great; for if we assign to nitrogen the atomic weight 7, and to chlorine 17.69, we could write the formula of the compound NH_2Cl, and this compound would have the molecular weight 26.69, as determined by Avogadro's method. On the other hand, if 7 be the atomic weight of nitrogen, and 17.69 that of chlorine, then in all other compounds of nitrogen or chlorine, in which one atom has been supposed to exist in the molecule, we must necessarily accept the existence of two atoms in the molecule. But then all these compounds would not come under Avogadro's rule. Hence we see that the compound NH_4Cl is clearly an exception, and, if no satisfactory explanation can be found to account for this case, its existence is fatal to the rule. A satisfactory explanation can be offered, however, as follows:—

If it can be proved that the vapor obtained from the compound NH_4Cl is not the vapor of this compound, but a mixture of the vapors of its constituents, ammonia, NH_3, and hydrochloric acid, HCl, the case becomes a very simple one. Without entering into details, it may be mentioned that the results of the experiments made upon this subject have justified the assumption that, when the compound NH_4Cl is heated to a temperature sufficiently high to convert it into vapor, it is broken down into its constituents, ammonia, NH_3, and hydrochloric acid HCl, and

that, when this mixture is cooled down, the two constituents again unite to form the original compound.

As ammonia, NH_3, and hydrochloric acid, HCl, combine volume to volume, so the mixture of the two gases, obtained by heating ammonium chloride, NH_4Cl, consists of equal volumes of the two; and the specific gravity of this mixed vapor should be the mean of the specific gravities of its constituents. The specific gravity of ammonia is 0.597, that of hydrochloric acid is 1.247; the specific gravity of a mixture of the two would be $\frac{0.597 + 1.247}{2} = 0.922$; and this specific gravity, if it be that of a chemical compound, leads to the molecular weight 26.6. The number 0.922 is, indeed, that found as the specific gravity of the vapor of ammonium chloride, and it will thus be seen that the fact can be satisfactorily explained without giving up our belief in Avogadro's law.

The compound phosphorus pentachloride, PCl_5, was also at one time regarded as an exception to the rule. The specific gravity of its vapor was found to be 3.66, from which the molecular weight 105.7 was calculated, half that required by the formula PCl_5. It has been shown, however, that above a certain temperature the molecule of this compound breaks down into a molecule of phosphorus trichloride, PCl_3, and a molecule of chlorine, Cl_2. The vapor from phosphorus pentachloride, PCl_5, is a mixture of two vapors, and the mean specific gravity of the two is the specific gravity found. The specific gravity of the vapor of the trichloride, PCl_3, is 4.88; that of chlorine is 2.45; mean specific gravity $\frac{4.88 + 2.45}{2} = 3.666$. In this case it has been shown further that the breaking down of the molecule takes place gradually; for the specific gravity of the vapor decreases from 5.08 to 3.66, as the temperature is raised from 182° to 300°, at which latter temperature the decomposition appears to be complete, no further decrease in specific gravity being observed when the vapor is heated still higher.

It has also been shown that when the specific gravity of the vapor of phosphorus pentachloride, PCl_5, is determined in the presence of the trichloride, PCl_3, the decomposition does not take place, and the specific gravity

found is that which theory requires for a compound of the formula PCl_5. The mean result of 7 determinations was 7.226, whereas, the theory requires 7.217. From this it is evident that the hypothesis of Avogadro is as valid for the compound PCl_5 as for other compounds.

A third example of this kind of decomposition by increase of temperature is met with in the case of the compound NO_2. This compound, at a low temperature, consists of colorless crystals. At a slightly elevated temperature these crystals change to a yellow liquid. The liquid boils at 20–30°, and is then converted into a gas of a reddish-brown color, and as the temperature of the gas is raised, the intensity of the color increases. The specific gravity of the gas decreases with this elevation of temperature; hence, it is supposed that the compound, at a low temperature, is properly represented by the formula N_2O_4, but that the molecule is broken down by heat, two molecules of NO_2 being formed. The latter is strongly colored, and the more of it there is present in the mixture, the more intense is the color of the gas.

Among chemical compounds there are few that conduct themselves like the three just described. As regards some of these, good proof can be given of the fact that their molecules are broken down by conversion into vapor, and, hence, the apparently abnormal specific gravities observed for these vapors find a simple explanation. As regards others, although positive proof to the same effect may indeed be lacking as yet, still strong indications are presented that the abnormal densities are due to the same cause. So that, up to the present, not only is no fact known that speaks strongly against Avogadro's hypothesis, but, on the contrary, new developments are constantly tending to strengthen it. It forms, to-day, by far the most reliable means for the determination of molecular weights of compounds and elements; and we have seen how, indirectly, it aids us in determining atomic weights. But, in order that it may be useful, it is necessary that the compound which we may desire to study, shall be capable of conversion into vapor, or, if it be an element under consideration, that at least one of the compounds of this element be gaseous or volatile. Only a comparatively small number of compounds satisfy these conditions, and of the 67 elements,

only 36 (see List, pp. 48-52) enter into the composition of these compounds. With no other means, then, at our command, the work would be incomplete. It is desirable that some other method should be introduced which shall be applicable to those elements not covered by Avogadro's rule, *i. e.*, those elements which are themselves incapable of conversion into vapor, and which do not enter into the composition of gaseous or volatile compounds.

CHAPTER IV.

A STUDY OF SOLUTIONS.

THE phenomena of solution have long been the subject of study, but not until the last few years have results been reached that were of importance in connection with the problem of the determination of molecular weights. Through the labors of Raoult, Pfeffer, Van't Hoff, and others, relations have been discovered between the freezing-point, the boiling-point, and the osmotic pressure of solutions on the one hand, and the molecular weights of the dissolved substances on the other.

Relation between the vapor-pressure of solutions and the molecular weights of the dissolved substances.—Although some generalizations were established by the study of water solutions, it was not until Raoult (1886) investigated ether solutions, that the connection between the vapor-pressures of solutions and the molecular weights of the dissolved substances was discovered. The principal conclusion to be drawn from these investigations may be stated thus: If $n =$ the number of molecules of the dissolved substance, $N =$ the number of molecules of the solvent, $p =$ vapor-pressure of pure ether, $p' =$ vapor-pressure of an ethereal solution, then

$$\frac{p - p'}{p} = c \frac{n}{N + n},$$

where c is a constant which falls between .96 and 1.09. The law may also be stated thus:—

> *The relative lowering of vapor-pressure is proportional to the ratio of the number of molecules of the dissolved substance to the total number of molecules in the solution.*

The relation expressed by this law plainly furnishes a new method for the determination of molecular weights. In this case it is not necessary that a substance should be capable of conversion into vapor; it is only necessary that

it should be soluble in a solvent for which the law has been found to hold good.

In practice it has been found most convenient to make observations on the boiling-points of solutions, and a method has been devised based upon such observations. Ether is most frequently used as the solvent.

Relation between the freezing-points of solutions and the molecular weights of the dissolved substances.—The researches of Raoult on the freezing-points of solutions led him to the discovery of the following law:—

> "*One molecule of any compound, when dissolved in* 100 *molecules of a liquid, lowers the freezing-point of the liquid by an amount which is nearly constant, viz.*, .62°."

Let P = weight of substance dissolved;
L = weight of solvent;
M = molecular weight of solvent;
E = reduction in freezing-point;
m = molecular weight of the dissolved substance.

Then

$$\frac{P}{L} : \frac{m}{100\ M} :: E : 0.62^\circ ,$$

or,

$$m = \frac{P \times 62\ M}{L \times E} .$$

For most so-called inorganic salts this law does not hold good, as will be pointed out more fully below. But it does hold for many classes of organic compounds and organic solvents. Glacial acetic acid and benzene are most commonly used as solvents.

The method of Raoult for the determination of molecular weights, based upon observations on the freezing-points of solutions, has come into extensive use since the year 1888.

Relation between the osmotic pressure of solutions and the molecular weights of the dissolved substances.—During the last century it was observed that, if a vessel be filled with alcohol and the vessel tightly covered by tying a bladder over its mouth, and the whole then immersed in water, the bladder is stretched outwards, showing that liquid from without has found its way within the vessel through the bladder. For many years investigations on

phenomena of this kind were carried on, but no results of a general character were reached until recently. In a book entitled "*Osmotische Untersuchungen*," published in 1877, Pfeffer, a botanist, gave an account of a large number of experiments, and laid the foundation of our present knowledge of the laws of osmotic phenomena. The simplest phenomenon of this kind is seen when a wide glass tube, tightly closed with a piece of bladder at the lower end, is partly filled with alcohol and then placed in a vessel of water, so that the level of the liquids inside and outside the tube is the same. If the tube be fixed in this position, the liquid is soon found to be rising in the tube. There is pressure from without inward. This is called *osmotic pressure*. Pfeffer's investigations had to do with the measurement of the pressure exerted by different substances under different conditions of temperature and dilution. Instead of using a bladder, which is not capable of much resistance, he used membranes made by precipitating copper ferrocyanide in the pores of clay-cells. Somewhat later, Van't Hoff showed that the results obtained by Pfeffer led to the following remarkable laws governing osmotic pressure:—

1. "*The pressure is proportional to the concentration, or it is inversely proportional to the volume in which a definite quantity of the dissolved substance is contained.*"

2. "*The pressure increases, for constant volume, proportionally to the absolute temperature.*"

3. "*Quantities of dissolved substances which are in the ratio of the molecular weights of these substances exert equal pressure at equal temperatures.*"

These laws are analogous to the well-known laws of gases, the third being plainly the analogue of the law of Avogadro. Another form of stating the third law, together with an extension of it, is this:—

Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.

Notwithstanding the simplicity of this law, no practical method of determining molecular weights based upon it has yet been devised. The difficulties are, however, mostly of an experimental nature.

Since Pfeffer's observations were published, other meth-

ods of determining osmotic pressure have been worked out, and the results obtained have been found to agree with those obtained by Pfeffer. Prominent among these methods is that of de Vries. It depends upon observations on organic cells in solutions of different concentrations. When such a cell containing protoplasm is introduced into a solution it will change its form perceptibly unless the osmotic pressure of the solution is the same as that of the contents of the cell. By changing the concentration of the solution it can be brought to such a condition that the cell retains its original form. By this means, it is possible to compare different solutions and to determine the concentration of the solutions that exert the same osmotic pressure.

Exceptions to the Laws of Solutions.—The laws governing the relations between the molecular weights of a dissolved substance and the freezing-point, boiling-point, and osmotic pressure of the solution are found not to hold good for water solutions of salt, strong acids, and bases. Such solutions act as if they contained a larger number of molecules than is indicated by their formulas. Thus in a dilute solution of sodium chloride there appear to be two molecules for every molecule of the substance added. To account for this it has been suggested by Arrhenius that, in these cases, the dissolved substances are separated into their *ions* by the action of the solvent. A similar suggestion had been previously made by Williamson and by Clausius for entirely different reasons. The solutions that give the peculiar results, that is, the water solutions of salts, and strong acids and bases, differ from other solutions in this respect that they are good conductors of the electric current, and this conduction is accompanied by a movement of the particles of the dissolved substance which is separated into its ions. According to the conception of Clausius and Arrhenius, then, when a salt is dissolved in water it is separated to some extent into its ions by the action of the water, the greater the dilution the more complete the separation. Under ordinary conditions these ions remain in the solution highly charged with electricity. As they move through the solution they come in contact with each other, and combinations and decompositions are constantly taking place. When such a solution is made part of an electric circuit, the electricity directs these ions, those charged with positive electricity in one direction

towards one pole, those charged with negative electricity towards the other pole. As soon as an ion reaches its proper pole its electricity is discharged and it is set free.

It will be seen that the hypothesis of dissociation in solution accounts for the results obtained in studying the freezing-points, etc., of water solutions, in much the same way that the peculiar results obtained in studying the vapor-densities of ammonium chloride and of phosphorus pentachloride are explained by the assumption that these substances undergo dissociation when heated.

The hypothesis of Arrhenius is still under discussion, though it has rapidly grown in favor during the past few years, and, apparently, those who have given most time to the study of the phenomena to which it applies, and who therefore are best qualified to pass judgment upon it, are the ones who receive it most cordially.

CHAPTER V.

EXAMINATION OF SOLID ELEMENTS AND COMPOUNDS.

Specific Heat.—It is known that, when equal weights of different substances are exposed to heat from the same source, they have different temperatures at the end of the same period of time. From this it is clear that to raise equal weights of different substances through the same number of degrees of temperature, different quantities of heat are necessary. Given exactly the same heating power, it takes about 32 times as long to raise the temperature of a pound of water 10, 20, or 30 degrees as it takes to raise the temperature of a pound of mercury the same number of degrees; or it takes 32 *times as much heat* to raise the temperature of a pound of water 10, 20 or 30 degrees as it takes to raise the temperature of a pound of mercury the same number of degrees. The quantity of heat required to raise the temperature of a given weight of any substance a given number of degrees, as compared with the quantity of heat required to raise the temperature of the same weight of water the same number of degrees, is called the specific heat of the substance. The quantity of heat required to raise the temperature of a pound of water 1 degree Centigrade may be conveniently adopted as the thermal unit. The specific heat of water is then = 1; and the specific heat of any other substance is the relative quantity of heat necessary to raise the temperature of a pound of this substance 1 degree Centigrade, taking the above thermal unit as the standard. The specific heat of mercury, according to the results of the experiment mentioned, is 0.03332; that of gold is found to be 0.03244, etc., etc. The meaning of these numbers will be readily understood.

Relations between Specific Heat and Atomic Weight.—Now, when the solid elements are examined with reference

to their specific heats, a very simple relation is found to exist between the numbers expressing the specific heats and the atomic weights. This relation will be made clear by the following examples:—

Element.	Specific heat.	Atomic weight.
Silver	0.0570	107.66
Zinc	0.0955	64.88
Cadmium	0.0567	111.7
Copper	0.0952	63.18
Tin	0.0562	117.4

It will be seen by an examination of this table that the atomic weights are inversely proportional to the specific heats. We have

$$107.66 : 64.88 :: 0.0955 : 0.0570;$$
$$111.7 : 63.18 :: 0.0952 : 0.0567;$$
$$107.66 : 117.4 :: 0.0562 : 0.0570, \text{ etc.}$$

These proportions are only approximately correct; but it must be remembered that the means for the determination of atomic weights and specific heats are not perfect, and in both sets of figures there are probably some slight errors. Hence, such slight variations from absolute agreement in these proportions are not surprising. The agreement is sufficiently close to indicate a close connection between the two sets of numbers. This connection may be stated in another way: The product of the atomic weight by the specific heat is a constant quantity for the elements examined. Thus, in the above cases:

$$107.66 \times 0.057 = 6.14$$
$$64.88 \times 0.0955 = 6.20$$
$$111.7 \times 0.0567 = 6.33$$
$$63.18 \times 0.0952 = 6.01$$
$$117.4 \times 0.0562 = 6.51$$

For the same weights, then, the quantities of heat necessary to elevate the temperature of the elements one degree vary. The quantity necessary to elevate the temperature of an atom one degree is, of course, represented by the variable quantity multiplied by the atomic weight, and this product, in the cases cited, is a constant.

Investigations of Dulong and Petit.—In the year 1819 attention was first called to the above relation by Dulong and Petit, and having examined a large number of ele-

ments they felt justified in propounding the law: *The atoms of all elements have the same capacity for heat.* This is simply a generalization from the facts stated, and is another way of stating that, to raise the temperature of an atom one degree, the same quantity of heat is always necessary.

If the law propounded is in reality a law, it will readily be seen that a new method is given for the determination of the atomic weights of elements of which we can determine the specific heat. If the constant obtained by multiplying the specific heats by the atomic weights is 6.25, which is about the average of the different values found, then it is plain that, if this number be divided by the specific heat of an element, a number will be obtained which will approximately represent the atomic weight. If A represent the atomic weight, and H the specific heat, the following formula expresses the relation:

$$A = \frac{6.25}{H}$$

In order that this might hold good for all the elements investigated by Dulong and Petit, they found it necessary to change the atomic weights of four of the metals; just as it had been necessary to change certain of the atomic weights in order that Avogadro's hypothesis might hold good in all cases. But as these atomic weights rested upon a questionable basis, there could be no serious objection to the change. Notwithstanding the simplicity of the law, its validity was not immediately acknowledged.

Investigations of Neumann and Regnault.—Twelve years later (1831) Neumann published investigations on the specific heat of chemical compounds, and showed that, for compounds of similar composition, the specific heats are inversely proportional to the molecular weights of the compounds, or the molecules of different compounds have equal capacity for heat; *i. e.*, for compounds of similar composition, the product of the molecular weight (M) by the specific heat (H) is a constant quantity. For example, the specific heat of lead iodide is 0.0427; that of lead bromide is 0.0533; that of lead chloride is 0.0664; the molecular weights of these compounds are respectively

459.48, 365.92, and 277.14. The products $M \times H$ are as follows:—

For lead iodide,	. .	$459.48 \times 0.0427 = 19.62$
" bromide,	. .	$365.92 \times 0.0533 = 19.50$
" chloride,	. .	$277.14 \times 0.0664 = 18.40$

Further, the specific heat of barium chloride is 0.0902; that of strontium chloride is 0.1199; that of calcium chloride is 0.1642. The molecular weights of these compounds are respectively 207.64, 158.04, and 110.65. The products $M \times H$ are:—

For barium chloride,	. .	$207.64 \times 0.0902 = 18.73$
" strontium chloride,	. .	$158.04 \times 0.1199 = 18.95$
" calcium chloride,	. .	$110.06 \times 0.1642 = 18.07$

Subsequently, similar investigations were carried out in connection with a large number of compounds, and it is particularly to the labors of Regnault (1840) that the development of this branch of the subject is due. The result attained may be stated concisely thus: *The elements possess essentially the same specific heat, whether they exist in a free state or in combination.*

To show how this conclusion may be drawn from known facts, let us take again the case of lead iodide. Lead has the specific heat 0.0307, iodine 0.0541. Multiplying by the atomic weights, we have $0.0307 \times 206.4 = 6.34$; and $0.0541 \times 126.54 = 6.85$; but, as can be determined, there are two atoms of iodine in the molecule of lead iodide, hence the atomic heat 6.85 must be multiplied by 2, which gives 13.70. To raise the constituents of lead iodide one degree in temperature would then require an amount of heat represented by the number $6.34 + 13.70 = 20.04$, and we have found that the amount of heat necessary to raise lead iodide as a compound one degree in temperature is 19.62. As these figures are practically identical, it follows that the specific heat of the elements in this case is the same, whether the elements are in combination or in the free state.

Determination of Atomic Weights by a Study of the Specific Heat of Compounds.—It thus appears that a study of the specific heat of compounds may be of assistance in the determination of atomic weights; for the specific heat of an element can be ascertained, even where this

cannot be determined directly. It is difficult, for instance, to ascertain the specific heat of gaseous elements directly, and yet, as these elements form solid compounds, the specific heat of the latter can be determined, and thus, indirectly, that of the gaseous elements.

To illustrate by an example, take the case of chlorine. Suppose it be required to determine the atomic weight of this element by means of specific heat determinations. We cannot determine the specific heat of the element directly. It forms compounds, however, with other elements, the specific heats and atomic weights of which can be determined. It combines with lead. The specific heat of lead is 0.0307, which, according to the law of Dulong and Petit, gives the atomic weight 206.4. Now, in lead chloride, 206.4 parts by weight of lead are combined with 70.74 parts by weight of chlorine; or, with 1 atom of lead there is combined an amount of chlorine weighing 70.74 times as much as 1 atom of hydrogen. But we do not know how many atoms of chlorine this weight represents. It cannot be less than one, but it may be 2, 3, 4, or more atoms. We determine the specific heat of lead chloride, and find it to be 0.0664. We have assumed that the molecular heat of a compound (*i. e.*, the product of the molecular weight by the specific heat) is equal to the sum of the atomic heats (*i. e.*, the product of the atomic weight by the specific heat) of the atoms contained in the compound; or

$$M \times H = A \times H + A' \times H' + A'' \times H'' \ldots .$$

But, as the products $A \times H$, $A' \times H'$, $A'' \times H''$ have been shown to be constant and equal to about 6.25, this equation becomes—

$$M \times H = n6.25;$$

and from this equation, M and H being known, the value of n, or the number of atoms contained in the molecule can be deduced.

In the case under consideration—

$$277.14 \times 0.0664 = n6.25;$$
$$18.40 = n6.25;$$
$$n = 3.$$

The conclusion is, therefore, drawn that in the molecule (277.14 parts) of lead chloride there are contained three

atoms. But we know that there is one atom of lead; hence, there must be two atoms of chlorine; and, as two atoms weigh 70.74, the atomic weight of chlorine is 35.37, the same as that found by means of Avogadro's method.

Further, there are other compounds in each of which 70.74 parts of chlorine are combined with a certain quantity of another element, and the molecular heat of which is the same as that of lead chloride. From the latter fact we conclude that there are also three atoms contained in the molecules of these compounds, and, hence, that quantity of an element which, in these compounds, is combined with 70.74 parts of chlorine, represents the atomic weight. Thus, the molecular heats of barium, strontium, and calcium chlorides are 18.73, 18.95, and 18.07 respectively, numbers which are practically identical with 18.40, the molecular heat of lead chloride; and in these compounds there are 136.9 parts barium, 87.3 parts strontium, and 39.91 parts calcium, combined with 70.74 parts chlorine. The conclusion is, therefore, drawn that 136.9, 87.3, and 39.91 are respectively the atomic weights of barium, strontium, and calcium, although direct determinations of the specific heat have been made in only two of these cases.

The following tables (I.) of elements and (II.) of compounds contain the numbers actually obtained and the conclusions drawn from them. The numbers under H are those representing the specific heats of the elements; those under A are the atomic weights as determined by analytical methods, aided by the rule of Avogadro, or that of Dulong and Petit; finally, in the last column is the product of the atomic weight by the corresponding specific heat ($A \times H$), called, for convenience, the atomic heat. The atomic weights given in this table are those most commonly used, as for the purposes in view here they answer as well as the more accurate ones, and for purposes of calculation they are plainly more convenient.

	H.	*A.*	*A × H.*
Lithium	0.941	7	6.6
Sodium	0.293	23	6.7
Magnesium	0.250	24	6.0
Aluminium	0.214	27	5.8
Silicon	0.173	28	4.8
Phosphorus	0.174	31	5.4
Sulphur	0.178	32	5.7
Potassium	0.166	39	6.5
Calcium	0.170	40	6.8
Chromium	0.100	52.4	5.2
Manganese	0.122	55	6.7
Iron	0.114	56	6.4
Cobalt	0.107	59	6.2
Nickel	0.109	59	6.4
Copper	0.0952	63.1	6.0
Zinc	0.0955	65	6.2
Arsenic	0.0814	75	6.1
Selenium	0.0746	79	5.9
Bromine (solid)	0.0843	80	6.7
Molybdenum	0.0722	96	6.9
Ruthenium	0.0611	103.5	6.3
Rhodium	0.0580	104.1	6.0
Palladium	0.0593	106.2	6.3
Silver	0.0570	108	6.2
Cadmium	0.0567	112	6.4
Indium	0.0570	113.4	6.5
Tin	0.0562	117.4	6.6
Antimony	0.0508	120	6.1
Iodine	0.0541	126.5	6.8
Tellurium	0.0474	125	5.9
Tungsten	0.0334	184	6.1
Gold	0.0324	197	6.4
Platinum	0.0324	194.3	6.3
Iridium	0.0326	192.5	6.3
Osmium	0.0311	195	6.1
Mercury	0.0317	200	6.3
Thallium	0.0335	204	6.8
Lead	0.0307	207	6.4
Bismuth	0.0308	207.3	6.5

The following are some of the compounds that have been employed for the purpose of determining the atomic weights of elements. The numbers under *H* are those representing the specific heats of the compounds; those under *M* are the molecular weights; the products $M \times H$

are the so-called molecular heats; n represents the number of atoms in the molecule of the compound:—

	$H.$	$M.$	$M \times H.$	$n.$	$\frac{M \times H.}{n.}$
$CoAs_2$	0.0920	209	19.2	3	6.4
Ag_2S	0.0746	248	18.5	3	6.2
Cu_2S	0.1212	158.8	19.2	3	6.4
HgS	0.052	232	12.1	2	6.1
NiS	0.1281	91	11.6	2	5.8
PbS	0.053	239	12.7	2	6.4
SnS	0.0837	150	12.6	2	6.3
SnS_2	0.1193	182	21.7	3	7.2
$AgCl$	0.0911	143.5	13.1	2	6.6
$CuCl$	0.1383	98.9	13.7	2	6.9
KCl	0.1730	74.6	12.9	2	6.5
$LiCl$	0.2821	42.5	12.0	2	6
$NaCl$	0.2140	58.5	12.5	2	6.3
$BaCl_2$	0.0896	208	18.6	3	6.2
$CaCl_2$	0.1642	111	18.2	3	6.1
$SrCl_2$	0.1199	158.5	19.0	3	6.3
$HgCl_2$	0.0689	271	18.7	3	6.2
$MgCl_2$	0.1946	95	18.5	3	6.2
$MnCl_2$	0.1425	126	18.0	3	6.0
$PbCl_2$	0.0664	278	18.5	3	6.2

Exceptions to the Law of Dulong and Petit.—An examination of these tables shows that the product, $A \times H$, in the first, and the quotient, $\frac{M \times H}{n}$, in the second—although assumed to be constant in value—vary considerably from the mean value, 6.25. Some of the variations are, no doubt, due to errors of observation in consequence of the imperfections of the methods employed for the determination of specific heat. Indeed, in all the cases cited in the above tables the variations are hardly great enough to lead us to suspect the incorrectness of the law of Dulong and Petit. The elements carbon, boron, and silicon, however, give results that are not in harmony with the law as stated. This will be seen best by means of the following table, in which H is the specific heat; t, the temperature at which the determination was made; A, the atomic weight; and $A \times H$, the atomic heat. As these three elements form the most marked exceptions

to the law, all the more reliable determinations of their specific heats are given :—

	H.	t.	A.	A × H.
Carbon :				
a. Diamond . .	0.064	—50.5°	12	0.77
" . .	0.096	—10.6°	12	1.15
" . .	0.113	+10.7°	12	1.36
" . .	0.132	33.4°	12	1.58
" . .	0.153	58.4°	12	1.84
" . .	0.177	85.5°	12	2.12
" . .	0.222	140°	12	2.66
" . .	0.273	206.1°	12	3.28
" . .	0.303	247°	12	3.64
" . .	0.441	606.7°	12	5.29
" . .	0.449	806.5°	12	5.39
" . .	0.459	985°	12	5.51
b. Graphite . .	0.114	—50.3°	12	1.37
" . .	0.199	61.3°	12	2.39
" . .	0.297	201.6°	12	3.56
" . .	0.445	641.9°	12	5.34
" . .	0.467	977.9°	12	5.60
c. Charcoal . .	0.194	0° to 99.2°	12	2.33
" . .	0.239	0° to 223.6°	12	2.87
Silicon :				
Crystallized . .	0.136	—39.8°	28	3.81
" . .	0.170	+21.6°	28	4.76
" . .	0.183	57.1°	28	5.12
" . .	0.190	86°	28	5.32
" . .	0.196	128.7°	28	5.49
" . .	0.201	184.3°	28	5.63
" . .	0.203	232.4°	28	5.68
Boron :				
Crystallized* .	0.192	—39.6°	11	2.11
" . .	0.238	+26.6°	11	2.62
" . .	0.274	76.7°	11	3.01
" . .	0.307	125.8°	11	3.38
" . .	0.338	177.2°	11	3.72
" . .	0.366	233.2°	11	4.03

An examination of the above table shows that at ordinary temperatures the elements carbon, silicon, and boron

* As has been shown by Hampe, crystallized boron, whether the crystals be of the black or the yellow variety, is not the pure element. According to this chemist, the black crystals have the composition AlB_{12}, and the yellow crystals the composition $C_2Al_3B_{48}$.

do not follow the law of Dulong and Petit, as it has been stated. It will be seen, however, that as the temperature is raised, the specific heat becomes greater until finally, in the cases of carbon and silicon, a point is reached beyond which there is no marked change. Thus at 600° the specific heat of diamond is 0.441, and at 985° it is 0.449. That of silicon is 0.201 at 185°, and 0.203 at 332°. At these temperatures the elements obey the law of Dulong and Petit. In the case of boron it will be observed that the highest temperature at which a determination of the specific heat has actually been made is 233.2°. Assuming that the rate of increase above 230° is the same as the rate between —40° and 230°, the specific heat would become 0.50 at about 600°, and this is the figure required by the law. The above facts may be conveniently stated in this form: The specific heats of the elements carbon, silicon, and boron increase gradually from the lowest temperature to certain points, above which they remain practically constant. The point for carbon and boron is about 600°; that for silicon about 200°. At these temperatures, and above them, the elements have the following specific heats: carbon 0.46; boron 0.50; silicon 0.205. The products obtained by multiplying these figures by the atomic weights 12, 11, and 28 are 5.5, 5.5, and 5.8; so that carbon, boron, and silicon are not exceptions. The law of Dulong and Petit, however, is a little more complicated than as stated above, and should have the following form:—

The specific heats of the elements vary with the temperature; but for every element there is a point, T, above which the variations are very slight. The product of the atomic weight by the constant value of the specific heat is nearly a constant, lying between 5.5 and 6.5.

Results similar to those above discussed have been obtained by Nilson, Pettersson, and Humpidge in the case of beryllium.

To account for the variations in the specific heats of the elements, it has been suggested that in most cases we cannot determine the true specific heat. This is only that heat which goes to increase the temperature. In measuring specific heats we have to deal with a complex quantity, viz., that heat which raises the temperature, together with that which performs internal work and that which performs external work. In the case of solids and liquids the ex-

ternal work performed is very small. The internal work is probably different in different cases, and may amount to considerable. The fact that the specific heats of so many elements, when multiplied by the atomic weights of these elements, give the same product, indicates that in these cases the internal work, like the specific heat, is inversely proportional to the atomic weights. It is evident, according to this, that, if the amount of internal work varies in different elements, the specific heat will also vary in such a way as to seem to conflict with the law. It remains, then, for the future to show how specific heat determinations can be made which shall be independent of the internal and external work. When this can be done, it is probable that the law of Dulong and Petit will be found to be a perfect law without exceptions.

ISOMORPHISM AS FURNISHING A MEANS FOR DETERMINING ATOMIC WEIGHTS.—Another means, once considered valuable, for determining atomic weights is found in the phenomena of isomorphism. It has long been known that some substances of entirely different composition have approximately the same crystalline form. This was explained by Mitscherlich (1819) by supposing that an equal number of atoms in different molecules causes the same crystalline form. A little later he proposed the following law of isomorphism:—

> *An equal number of atoms, united in the same way, give the same crystalline form; and this crystalline form is independent of the chemical nature of the atoms, being only dependent on their number and arrangement.*

If this law were strictly true, it is plain that we should in many cases be able to determine atomic weights by its aid. A few examples will illustrate the method.

The two substances $BaCl_2+2H_2O$ and $BaBr_2+2H_2O$ are isomorphous. We may assume, then, that their molecules contain the same number of atoms, and, if we know the atomic weights of the constituents of the molecule $BaCl_2+2H_2O$, we can easily determine the atomic weight of the constituent bromine in the molecule $BaBr_2+2H_2O$. Further, the compounds CuAgS and CuCuS are isomorphous. If the molecules of each contain the same number of

atoms, and the atomic weights of copper and sulphur are known, the atomic weight of silver can be found.

This method has no doubt been of service in the determination of atomic weights. Nevertheless, it requires but a few examples to prove that, if to the term isomorphism we give the wide meaning implied in the wording of the law as stated above, the results reached by means of it are not reliable. The salts $BaMn_2O_8$,Na_2SO_4, and Na_2SeO_4 have the same crystalline form, and yet the best methods for determining formulas show that those given are probably correct. If we were, in these cases, to assume that the number of atoms in each of the molecules is the same, we should reach results at variance with those obtained by the most reliable methods. It will thus be seen that if the isomorphism of salts be employed as a method for the determination of atomic weights, the results must be looked upon as doubtful, unless the sense of the word isomorphism be restricted.

According to Kopp, identity of crystalline form is not a sufficient basis for designating compounds as isomorphous, and the term should be used in a much more restricted sense. If, according to this writer, a crystallized compound has the power of growing in a solution of another compound, then the two may be regarded as isomorphous. Thus, as is well known, if a crystal of ordinary alum be placed in a solution of iron alum, it will grow in the samė way that it would in the original solution. This power of forming *overgrowths* should be regarded as the true criterion of isomorphism. Understood in this sense, the use of the expression isomorphism becomes much more restricted than it was when used in the old sense. There are many compounds which have the same crystalline form which are not isomorphous in the new sense.

In the foregoing, free use has been made of the expression *Atomic weights*. Using the language of the atomic theory, the methods for determining the *Atomic weights* have been considered. It is well, however, before passing on to the next part of our subject to recall the fact that it cannot be positively asserted of the figures called atomic weights that they represent the relative weights of atoms. Whether they do or do not, they certainly have a close

relation to certain important facts that lie at the foundation of all cases of chemical action. The laws of definite and multiple proportions are the fundamental laws of chemistry. They are as firmly established as any laws of nature, and they are simply the expressions of facts observed. We can certainly select for each element a figure, which itself will represent, or a multiple of which will represent, the proportion by weight in which this element enters into chemical action. The difficulty is to know which one to select. To get over the difficulty we study certain physical properties of the elements and their compounds, as the specific gravity of the vapor, the specific heat, the crystalline form, and determine the weights of the substances which, on this basis, seem to be analogous. We thus get figures which bear to one another relations very similar to those which the so-called atomic weights, determined by chemical methods, bear to one another. The similarity of the relations of the figures obtained by the different methods suggests a common cause, and we attempt to satisfy our desire to ascertain the cause by saying that the figures represent the relative weights of atoms. But the figures would be just as valuable without this theory, and we might deal with all the facts of chemistry without referring to the possible existence of atoms. We shall next find that the atomic weights determined by the methods of Avogadro and Dulong and Petit are confirmed in a most striking way by an extremely important discovery, touching the relations which exist between the atomic weights of the elements and their properties.

CHAPTER VI.

PROPERTIES OF THE ELEMENTS AS FUNCTIONS OF THEIR ATOMIC WEIGHTS—THE PERIODIC LAW.

Natural Groups of Elements.—On examining the list of elements and their atomic weights, we find that there are a number of well-marked groups, indicating some connection between the atomic weights and properties of the elements. Among these may be mentioned chlorine, bromine, and iodine; sulphur, selenium, and tellurium; lithium, sodium, and potassium. Arranging these according to their atomic weights we have:—

Cl	35.37	S	31.98	Li	7.01
Br	79.76	Se	78.87	Na	23
I	126.54	Te	125	K	39.03

If in each of these groups the atomic weights of the first and last members be added together, and the sum divided by 2, very nearly the atomic weights of the middle members of the series are obtained: $\frac{35.37 + 126.54}{2} = 80.95$, $\frac{31.98 + 125}{2} = 78.49$, $\frac{7.01 + 39.03}{2} = 23.02$. It will be observed, also, that the elements, whose atomic weights are thus closely connected, are themselves very closely allied in their properties. Considerations of this kind have led chemists, from time to time, to examine the atomic weights more closely, and, as a result of these examinations, it has been found that the connection above indicated is much more general than was at first supposed. Attention was first called to the general character of the relations between the properties of the elements and their atomic weights by J. A. R. Newlands, in a number of papers which appeared in the years 1864–66, but, owing to some marked inconsistencies in his arrangement of the elements, the importance of the subject was not generally

recognized. Shortly afterward, in 1869 and 1870, two papers appeared, one by D. Mendelejeff* and the other by Lothar Meyer,† in which these relations were treated in a masterly manner, and it was then seen that one of the most important laws of chemistry had been discovered. Everything learned since then has only made it appear more and more certain that the *periodic law* is a fundamental law of chemistry.

Mendelejeff's Tables.—Mendelejeff first calls attention to the fact that, if all the light elements with atomic weights from 7 to 36‡ are arranged *in the order of their atomic weights*, the following remarkable table is obtained:—

Li = 7;	Be = 9;	B = 11;	C = 12;	N = 14;	O = 16;	Fl = 19;
Na = 23;	Mg = 24;	Al = 27;	Si = 28;	P = 31;	S = 32;	Cl = 35.5.

In these two series, elements which we recognize as similar come to stand together, as lithium and sodium, beryllium and magnesium, carbon and silicon, oxygen and sulphur, etc. The gradual change in the properties of the members of the series, as we pass from left to right, is noticed especially with respect to the compounds which the elements form. Thus, only the four last members combine with hydrogen, yielding compounds of the general formulas—

$$RH_4,\ RH_3,\ RH_2,\ RH.$$

The character of these hydrogen compounds also changes gradually, according to the position in the series. Hydrochloric acid, HCl, is a marked acid of great stability; hydrogen sulphide, H_2S, is a weak acid decomposable by heat; phosphine, PH_3, is not an acid, and is less stable than the preceding compounds, and silicon hydride, SiH_4, is still less stable than phosphine, PH_3.

The oxides of the members of the second series form this series—

$$Na_2O,\ \underset{\text{or } MgO,}{Mg_2O_2},\ Al_2O_3,\ \underset{\text{or } SiO_2,}{Si_2O_4},\ P_2O_5,\ \underset{\text{or } SO_3.}{S_2O_6},\ Cl_2O_7,$$

* Zeitschrift für Chemie, 1869, 405; and Annalen der Chemie, 8 Suppl., 133.

† Annalen der Chemie, 7 Suppl., 356.

‡ *To avoid unnecessary complications, the ordinary atomic weights are used in the treatment of this subject.*

From left to right in this series the basic properties grow weaker and the acid properties stronger. Again, in the composition of the hydroxides a similar regularity is observed—

$$Na(OH),\ Mg(OH)_2,\ Al(OH)_3,\ Si(OH)_4,\ PO(OH)_3,\ SO_2(OH)_2,\ ClO_3(OH).$$

Another point to be noted is this: that, in the series with which we are dealing, the metals are at one end and the so-called non-metals at the other, while those elements which are sometimes classed with the metals and sometimes with the non-metals, as, for instance, silicon, come in the middle.

But just as the chemical properties undergo gradual change in the series mentioned, so, also, a corresponding change is noticed in the physical properties. To illustrate this, the specific gravities and the atomic volumes of the members of the second series are given:—

	Na	Mg	Al	Si	P	S	Cl
Spec. gr.	0.97	1.75	2.67	2.49	1.84	2.06	1.33
Atom. vol.	24	14	10	11	16	16	27

	Na_2O	Mg_2O_2	Al_2O_3	Si_2O_4	P_2O_5	S_2O_6	Cl_2O_7
Spec. gr.	2.8	3.7	4.0	2.6	2.7	1.9	?
Atom. vol.	22	22	25	45	56	82	?

Another series corresponding to the two already given is the following:—

	Ag = 108;	Cd = 112;	In = 113;	Sn = 118;	Sb = 120;	Te = 125;	I = 127
Sp. gr.	10.5;	8.6;	7.4;	7.2;	6.7;	6.2;	4.9.

All the elements may be arranged in series similar to the above, and thus a very intimate connection between the atomic weights and the properties of the elements is shown to exist. It will be noticed that the changes in the properties of the elements are *periodic*. First, these properties change according to the increasing atomic weights, then they are repeated *in a new period* with the same regularity as in the preceding series. Such series as those already mentioned are called *small periods*. If hydrogen is placed in the first series, then lithium, etc., come in the second series, sodium, etc., in the third, etc.

But all the known elements cannot be arranged in the small periods, and what is much more important, the corresponding members of the even (4, 6, etc.) periods, or of the uneven (5, 7, etc.) resemble one another more closely

than the members of the even periods resemble those of the uneven periods. This is seen from the following—

Fourth period:	K,	Ca,	Sc,	Ti,	V,	Cr,	Mn.
Fifth " :	Cu,	Zn,	Ga,	Ge,	As,	Se,	Br.
Sixth " :	Rb,	Sr,	Y,	Zr,	Nb,	Mo,	—
Seventh " :	Ag,	Cd,	In,	Sn,	Sb,	Te,	I.

The members of the fourth and sixth periods resemble one another more closely than they resemble the members of the fifth or seventh periods; and the members of the fifth and seventh periods resemble one another closely. The last members of the even periods resemble in many respects the first members of the succeeding uneven series. Thus chromium and manganese in their basic oxides are similar to copper and zinc. On the other hand, between the last members of the uneven periods and the first members of the succeeding even periods, there are very marked differences, as, for instance, between bromine and rubidium. Further, between the last members of the even periods and the first members of the uneven periods, all those elements which cannot be arranged in the small periods would, according to their atomic weights and properties, naturally come. Thus, between chromium and manganese, on the one hand, and copper and zinc on the other, iron, cobalt, and nickel would come; the following series being thus formed:—

$$Cr = 52;\ Mn = 55;\ Fe = 56;\ Co = 58;\ Ni = 59;\ Cu = 63;\ Zn = 65.$$

As iron, cobalt, nickel follow the fourth period, so ruthenium, rhodium, palladium follow the sixth period, osmium, iridium, platinum follow the tenth period. Two small periods (an even and uneven), together with an intermediate series of the elements just mentioned, form a *large period*. As the intermediate members mentioned correspond to none of the seven small periods, they form an independent eighth group:—

Fe = 56;	Co = 58;	Ni = 59,
Ru = 101;	Rh = 103;	Pd = 106,
Os = 191;	Ir = 192.5;	Pt = 194.3.

The members of this group resemble one another in the same way as the corresponding members of the even

periods, as, for instance, vanadium, niobium, tantalum, or chromium, molybdenum, tungsten and others.

The two following tables of Mendelejeff show clearly the relations described. In the first, the elements with their atomic weights are arranged in large periods; in the second, they are arranged in groups and series in such a manner as distinctly to indicate the differences between the even and uneven periods.

Series.	Group I. — R_2O	Group II. — RO	Group III. — R_2O_3	Group IV. RH_4 RO_2	Group V. RH_3 R_2O_5	Group VI. RH_2 RO_3	Group VII. RH R_2O_7	Group VIII. — RO_4
1	H = 1							
2	Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	Fe = 19	
3	Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	Sc = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 58, Ni = 59, Cu = 63
5	(Cu = 63)	Zn = 65	Ga = 70	Ge = 72	As = 75	Se = 79	Br = 80	
6	Rb = 85	Sr = 87	Y = 89	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 101, Rh = 103, Pd = 106, Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 120	Te = 125	I = 127	
8	Cs = 133	Ba = 137	La = 139	Ce = 142	Di = 145	—	—	— —
9	(—)	—	—	—	—	—	—	— —
10	—	—	Yb = 173	—	Ta = 182	W = 184	—	Os = 191, Ir = 193, Pt = 195, Au = 196
11	(Au = 196)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	— —
12	—	—	—	Th = 231	—	U = 240	—	— —

			I.	II.	III.	IV.	V.	VI.
R_2O	I.		Li = 7	K 39	Rb 85	Cs 133	— —	— —
RO	II.		Be = 9	Ca 40	Sr 87	Ba 137	— —	— —
R_2O_3	III.		B = 11	Sc 44	Y 89	La 139	Yb 173	— —
RO_2	IV.	(H_4C)	C = 12	Ti 48	Zr 90	Ce 142	— —	Th 231
R_2O_5	V.	(H_3N)	N = 14	V 51	Nb 94	Di 145	Ta 182	— —
RO_3	VI.	(H_2O)	O = 16	Cr 52	Mo 96	— —	W 184	U 240
R_2O_7	VII.	(HF)	F = 19	Mn 55	— —	— —	— —	— —
				Fe 56	Ru 101	— —	Os 191	— —
RO_4	VIII.			Co 59	Rh 103	— —	Ir 193	— —
				Ni 59	Pd 106	— —	Pt 195	— —
R_2O	I.	H = 1	Na = 23	Cu 63	Ag 108	— —	Au 196	— —
RO	II.		Mg 24	Zn 65	Cd 112	— —	Hg 200	— —
R_2O_3	III.		Al 27	Ga 70	In 113	— —	Tl 204	— —
RO_2	IV.	(H_4R)	Si 28	Ge 72	Sn 118	— —	Pb 207	— —
R_2O_5	V.	(H_3R)	P 31	As 75	Sb 120	— —	Bi 208	— —
RO_3	VI.	(H_2R)	S 32	Se 79	Te 125	— —	— —	— —
R_2O_7	VII.	(HR)	Cl 35.5	Br 80	I 127	— —	— —	— —

It is not necessary to point out here all the properties of the elements which have been shown to vary in harmony with the changes of the atomic weights. What has already been said will suffice to indicate the principle involved in the construction of the tables of Mendelejeff. Close study of these tables does undoubtedly show that they contain some imperfections and apparent contradictions; still, these are not numerous enough nor serious enough to interfere materially with the value of the tables. It is evident that the first condition for the construction of such tables is the correct determination of all the atomic weights. We have seen with what difficulty this determination is often attended, and how doubtful some of the results obtained are. When all the atomic weights shall have been accurately determined, and when all the properties, both physical and chemical, of the elements are known, then a table constructed on the principle of the

above will, in all probability, show a perfect accordance between atomic weights and properties.

Mendelejeff originally proposed to use the *periodic law*, as he calls the law governing the variations in the atomic weights and properties of the elements, for the purpose of determining the properties of undiscovered elements. When Table II. was first constructed, a member was wanting between calcium and titanium in the fourth series. The atomic weight of this element should be about 44, and its properties were also very nearly foretold from its position. Its oxide should have the composition R_2O_3, and its properties should bear the same relation to aluminium oxide, Al_2O_3, that those of calcium oxide, CaO, bear to magnesium oxide, MgO, or titanium oxide, TiO_2, to silicon dioxide, SiO_2. Consequently it should be a more energetic base than aluminium oxide, Al_2O_3, and should resemble it in corresponding compounds. Its sulphate should not be as easily soluble as aluminium sulphate, because calcium sulphate is more difficultly soluble than magnesium sulphate. Thus, throughout the whole list of properties, such comparisons were made, and the unknown element was more accurately described than some of those which have been known for a long time.

The prediction of this element, to which Mendelejeff gave the name ekaboron, proved to be one of the most remarkable predictions ever made in the field of chemistry. Within a few years the metal scandium was discovered, and was shown to be the predicted ekaboron. Before its discovery, in a similar way, gallium was predicted and described under the name of ekaluminium; and quite recently germanium has been discovered and shown to be the element needed to fill the gap between gallium and arsenic, the properties of which, under the name ekasilicon, were described by Mendelejeff nearly twenty years ago.

Such speculations are, without doubt, very attractive, but we must not forget that the tables, which are used as their foundation, are more or less imperfect, and hence the conclusions drawn must necessarily be doubtful. On the other hand, the time will come when such speculations can be indulged in without risk of reaching doubtful results. The approach of this time will be hastened by just such efforts as those of Mendelejeff to discover the law govern-

ing the connection between the atomic weights and the properties of the elements.

Lothar Meyer's Arrangement of the Elements.— Another arrangement of the elements showing the connection between the atomic weights and the properties of the elements is that of Lothar Meyer, already alluded to. His table* follows:—

I.	II.	III.	IV.	V.	VI.	VII.	VIII.		
Li 7.01	Be 9.08	B 10.9	C 11.97	N 14.01	O 15.96				
Na 23	Mg 24.3	Al 27.04	Si 28.3	P 30.96	S 31.98	F 19.06			
K 39.03	Ca 39.91	Sc 43.97	Ti 48	V 51.1	Cr 52.45	Cl 35.37			
Cu 63.18	Zn 65.10	Ga 69.9	Ge 72.3	As 74.9	Se 78.87	Mn 54.8	Fe 55.88	Co 58.6	Ni 58.6
Rb 85.2	Sr 87.3	?Y 88.9	Zr 90.4	Nb 93.7	Mo 95.9	Br 79.76			
Ag 107.66	Cd 111.7	In 113.6	Sn 118.8	Sb 119.6	Te 125	? 98	Ru 101.4	Rh 102.7	Pd 106.35
Cs 132.7	Ba 136.9	La 138	Ce 139.9	Di? 145	? 151	I 126.54			
? 165	? 170	Yb 172.6	? 176	Ta 182	W 183.6	? 152			
Au 196.7	Hg 199.8	Tl 203.7	Pb 206.4	Bi 207.3	? 210	? 185	Os 191	Ir 192.5	Pt 194.3
? 222	? 226	? 230	?Th 232	? 234	?U 239	? 211			

This table contains all the elements whose atomic weights have been determined with any degree of certainty. The

* Die modernen Theorien der Chemie, Fünfte Auflage. Breslau, 1884.

essential difference between this arrangement and the first one of those of Mendelejeff given above consists in this, that the periods are arranged, not in horizontal lines, but in lines which are so inclined that, if the table were pasted on a cylinder of proper size, the table would have the form of a continuous spiral, beginning at the top with lithium and ending at the bottom with uranium. Meyer further points out the connection between the atomic weights and the following properties of the elements: specific gravity in the solid condition, as shown by a comparison of the atomic volumes; metallic ductility, fusibility, and volatility; crystalline form; influence upon the refraction of light; specific heat; conducting power for heat and electricity. The connection is shown to be a remarkably close one. For a further study of this subject the student is referred to Lothar Meyer's masterly book, "Die modernen Theorien der Chemie."

CHAPTER VI.

VALENCY.

Definition.—The methods for the determination of the molecular formulas of compounds have been discussed. By applying these methods expressions are obtained for the composition of compounds which, in all probability, are relatively correct. If the formulas as determined be now compared, certain regularities will appear. A few examples among the hydrogen compounds will serve the purpose.

I.	II.	III.	IV.
ClH,	OH_2,	NH_3,	CH_4,
BrH,	SH_2,	AsH_3,	SiH_4.
IH,	SeH_2,	SbH_3,	
FH,	TeH_2,	PH_3,	

It will be seen that chlorine, bromine, iodine, and fluorine combine with hydrogen in the proportion of atom to atom; oxygen, sulphur, selenium, and tellurium combine with hydrogen in the proportion of two atoms of hydrogen to one atom of the other element; in the compounds with nitrogen, arsenic, antimony, and phosphorus, three atoms of hydrogen are in combination with one atom of the other element; and, lastly, four atoms of hydrogen are in combination with one atom of carbon and of silicon. No elements are known which combine with a larger proportion of hydrogen than carbon and silicon. It is clear, therefore, that those elements which combine with hydrogen can be divided into four classes, the differences between which are shown by the examples given above. With reference to their power of combining with the halogens, elements differ from one another in a similar way. The following examples will make this clear:—

NaCl	$BaCl_2$	PCl_3	CCl_4	PCl_5	WCl_6
KCl	$CaCl_2$	$AsCl_3$	$SiCl_4$	$AsCl_5$	—
LiCl	$ZnCl_2$	$SbCl_3$	$SnCl_4$	$SbCl_5$	—.

There is greater diversity among the compounds with the halogens than among the compounds with hydrogen. While the largest number of hydrogen atoms with which any atom can combine is apparently four, the largest number of chlorine atoms with which any atom can combine is apparently six. The same is true of the other halogens. Turning now to the compounds of oxygen still greater diversity appears, as is seen in the following table:—

Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7	RuO_4
	(Mg_2O_2)		(Si_2O_4)		(S_2O_6)		(Ru_2O_8)
K_2O	CaO	Se_2O_3	TiO_2	V_2O_5	CrO_3	Mn_2O_7	OsO_4
	(Ca_2O_2)		(Ti_2O_4)		(Cr_2O_6)		(Os_2O_8)

The simplest compounds of oxygen are those in which one atom of this element is in combination with two atoms of some other elements. From the examples given above it will be seen that there are eight classes of oxygen compounds in which the oxygen combined with two atoms of the other elements varies from one to eight atoms.

In general, then, it may be said that the elements differ from one another as regards the complexity of the compounds which they can form with other elements.

But there must be some reason for the difference. Where shall we seek for it? If we accept the atomic hypothesis of Dalton, we must seek for the proximate causes of phenomena presented to us by masses of elements or their compounds in the atoms composing these masses. Here, then, we are to find in the atoms themselves the proximate cause of this new property of elements. As, however, we can learn nothing of atoms directly, but only of masses of atoms, it is evident that this cause cannot be discovered, but must finally be imagined, just as the atom itself is still only imagined to exist. In other words, our conception of atoms must become enlarged in such a way as to account for the new property, or a subordinate hypothesis must be framed to supplement the atomic hypothesis. Before framing this hypothesis, let us see whether we can learn anything more in regard to the new property than we have yet learned.

We have seen above that the molecules of some of the hydrogen compounds contain only 1 atom of hydrogen to each atom of the other element; in the molecules of other compounds we find 2 atoms of hydrogen to 1 atom of the

other constituent; in others 3, and in still others 4 atoms of hydrogen combined with 1 atom of some other element. In thus stating the number of atoms present in the molecules, we have, of course, left the domain of facts and have already entered that of hypothesis; still, the hypothesis involved in a molecular chemical formula, which has been determined by the aid of all means at our command, is one which we are justified in employing, and we consequently state the knowledge we have gained in terms of the hypothesis. Taking into consideration the sum total of our knowledge, as thus far stated, the simplest hypothesis which it is possible to form concerning the cause which we are striving to find, is the following: Every atom of an element has an inherent power of holding in combination a certain number of other atoms, this number being dependent upon the nature of the atoms held in combination. The simplest atoms represent the unit of this power, and we can distinguish between these simplest or unit-atoms and such as have the power of holding in combination 2, 3, 4, or more atoms.

Name of the New Property.—The property of the elements under consideration has, in accordance with the simple hypothesis just given, been termed *atomicity, quantivalence*, or only *valency.** The elements, which consist of the unit-atoms, are hence called *monatomic* or *univalent;* those consisting of atoms which have twice the combining power of the unit-atoms, are called *diatomic* or *bivalent;* and, in a similar manner, there are *triatomic* or *trivalent, tetratomic* or *quadrivalent*, etc., elements. Further, the

* In regard to the choice between the three expressions given, it may be said that the word valency seems to be less objectionable than the others which have been used, because it is the simplest, and, at the same time, it expresses all that it is desired to express with reference to the property which it designates. Again, the word atomicity has been used in another sense, and hence its use might lead to confusion, some authors employing it in its first sense, others in the new and entirely different sense. By a monatomic, diatomic, etc., element is sometimes meant an element whose molecule consists of 1, 2, etc., atoms. As it is necessary to have words to express this latter sense, it seems desirable to leave the word atomicity and its adjective derivatives, monatomic, diatomic, etc., to serve this purpose, while we adopt the expression valency with the derivatives univalent, bivalent, trivalent, etc., for the purpose of designating the property under discussion.

elements are called respectively *monads*, *dyads*, *triads*, *tetrads*, *pentads*, *hexads*, etc. Accordingly, of the elements in the brief table of hydrogen compounds, given at the beginning of this chapter (p. 88), those in the first line are univalent; oxygen, sulphur, selenium, and tellurium are bivalent; nitrogen, arsenic, antimony, and phosphorus are trivalent; and carbon and silicon are quadrivalent towards hydrogen.

Distinction between Valency and Affinity.—The property of valency must not be confounded with that of affinity. By affinity is usually meant the force with which one atom attracts another or others. Valency has apparently no connection with this force. An element may, in general terms, have a strong affinity for other elements, and yet be univalent. Another may possess but a weak affinity, and be quadrivalent. Thus, chlorine has a strong affinity for hydrogen; the two combine with great energy, yet they are univalent with reference to each other. While carbon does not combine with chlorine with nearly as great energy as hydrogen does, it is, nevertheless, quadrivalent towards hydrogen; its atom is capable of holding in combination 4 atoms of hydrogen. The two properties, valency and affinity, are possessed by every atom, and exhibit themselves every time that atoms act upon each other, the latter determining the energy of the action, the former the complexity of the resulting molecule.

Methods for Determining the Valency of the Elements.—The foundation upon which the conception of valency rests and the conception itself being thus explained, let us inquire how the valency of the individual elements is determined. The valency towards hydrogen of those elements which combine with it may first be determined. The first general rules to guide us in the measurements are the following:—

1. Those elements which combine with hydrogen in the proportion of 1 atom to 1 atom are univalent. Such, for instance, are chlorine, bromine, etc.

2. Those elements which combine with hydrogen in the proportion of 1 atom to 2 atoms of hydrogen are bivalent. Such, for instance, are oxygen, sulphur, etc.

3. Those elements which combine with hydrogen in the

proportion of 1 atom to 3 atoms of hydrogen are trivalent. Such, for instance, are nitrogen, phosphorus, etc.

4. Those elements which combine with hydrogen in the proportion of 1 atom to 4 atoms of hydrogen are quadrivalent. Such, for instance, are carbon, silicon, etc.

The next question to be answered is whether the valency of an element towards hydrogen is also its valency toward other elements, as the halogens, oxygen, etc. It requires but a cursory examination to show that this question must be answered in the negative, at least for several of the elements. Thus, while phosphorus forms the hydrogen compound, PH_3, and does not combine with hydrogen in larger proportion, it forms two compounds with chlorine, the trichloride, PCl_3, and the pentachloride, PCl_5. Sulphur forms with hydrogen the compound SH_2, in which it is bivalent, and it cannot combine with a larger proportion of hydrogen. On the other hand, it forms the compounds SCl_2 and SCl_4 with chlorine, and the simplest explanation of these is that in them the sulphur is respectively bivalent and quadrivalent. Taking carbon and silicon, however, we find that these elements have the same valency towards the halogens as toward hydrogen, as is shown by the compounds CH_4, SiH_4, CCl_4, and $SiCl_4$. As regards the valency towards oxygen it can be shown in the same way that in many cases it is not the same as the valency towards hydrogen. The fact that water has the composition H_2O shows that oxygen is bivalent. In sodium oxide, Na_2O, then, we have a compound analogous to water. In it the oxygen is probably bivalent. In such compounds as calcium oxide, CaO, magnesium oxide, MgO, in which one atom of oxygen is combined with one atom of another element, the elements are usually regarded as bivalent. In the same way when one atom of any element holds in combination two atoms of oxygen it is regarded as quadrivalent; and when one atom of any element holds in combination three atoms of oxygen it is regarded as sexivalent towards oxygen. An examination of the table of oxygen compounds given on page 89 will show that the valency of elements towards oxygen varies from 1 to 8. Sodium is univalent towards oxygen, magnesium is bivalent, aluminium trivalent, silicon quadrivalent, phosphorus quinquivalent, sulphur sexivalent, chlorine septivalent, and ruthenium octivalent. Other views

in regard to these oxygen compounds are possible, as will be shown below, and these other views have been generally held The above is, however, the most natural inference from the facts, and, unless it can be shown to be untenable, it must have the preference over more complicated views.

Comparing now the valency of a few elements towards hydrogen, with the valency of the same elements towards the halogens and towards oxygen, it will be found that in those cases in which a difference is observed the valency towards hydrogen is the lowest, and that towards oxygen the highest, while that towards chlorine is intermediate between these. Thus, sulphur is bivalent towards hydrogen, apparently sexivalent towards oxygen, and quadrivalent towards chlorine. Iodine is univalent towards hydrogen, apparently septivalent towards oxygen, as shown by the compound I_2O_7, but trivalent towards chlorine, and quinquivalent towards fluorine, as shown by the compounds ICl_3 and IF_5. But just as carbon and silicon are quadrivalent towards hydrogen and chlorine, so they are also quadrivalent towards oxygen, as shown in the compounds CO_2 and SiO_2.

While it appears clear from the above considerations that the power called valency is not the same towards different elements, it is further true that the valency of some elements varies towards one and the same element. Thus, it has been stated that phosphorus is trivalent towards hydrogen and quinquivalent towards chlorine; but that it is not always quinquivalent or that it does not always appear to be so, is shown by the compound PCl_3. So, too, while sulphur is bivalent towards hydrogen, quadrivalent towards chlorine, and sexivalent towards oxygen, it also appears to be bivalent towards chlorine, and quadrivalent towards oxygen, as shown by the compounds SCl_2 and SO_2. Chlorine, which is univalent towards hydrogen and septivalent towards oxygen, may also act as a univalent element towards oxygen, as is shown in the compound Cl_2O.

Is Valency Constant or Variable?—From what has already been said there would appear to be only one possible answer to this question. Valency is plainly variable, if we consider the composition of the compounds

which an element forms as final evidence of the valency of that element. If we consider valency as due to something residing in atoms, it is difficult to conceive of this something as being variable, any more than we can conceive of the weight of atoms as variable. How can one and the same atom have at one time the power to combine with one univalent atom, and at another time three or five times that power? If it has the power to combine with five univalent atoms once, it seems most natural to suppose that it will always have that power. Considerations of this kind have led to various hypotheses which have for their object the explanation of what appear to be variations in valency, on the supposition that valency is a constant property of atoms. There are two cases to be distinguished between: (1) *Those in which the valency of an element A varies towards one and the same element B; and (2) those in which the valency of an element varies according to the character of the element with which it combines.*

Variation of Valency towards one and the same Element.—Examples of this kind of variation of valency have already been given. Phosphorus appears to be trivalent and quinquivalent towards chlorine, and also towards oxygen, as shown by the compounds P_2O_3 and P_2O_5; sulphur is bivalent and quadrivalent towards chlorine; and quadrivalent and sexivalent towards oxygen, as shown by the compounds SO_2 and SO_3. Carbon is bivalent and quadrivalent towards oxygen, as is shown by the compounds CO and CO_2. Chlorine is at least univalent and trivalent towards oxygen, as is shown by the compounds Cl_2O and Cl_2O_3. The chief hypotheses which have been put forward to account for variations of the kind just mentioned will now be briefly presented.

Atomic and Molecular Compounds.—One of the first attempts to explain variations in valency was the hypothesis that there are two kinds of chemical compounds, the *atomic* and *molecular*. The former are the only true chemical compounds, in the sense in which that expression has been used from the beginning. In these, the atoms exhibit all the properties which have thus far been recognized as belonging to them—including valency.

By virtue of these properties, the compounds have their existence. In the molecular compounds, on the other hand, a new force is supposed to act, this force being distinct from the interatomic force, and acting in a peculiar way between molecules. The molecules are supposed to be first formed by means of chemical affinity, etc., and, when these have been formed, all that can be effected by valency has been effected. But now it is further supposed that the molecules thus formed have an attractive power and combining power of their own, by virtue of which the molecular compounds are formed. The most common examples of molecular compounds are salts containing water of crystallization. These are formed by virtue of the attraction of the molecules of the salt for the molecules of the water. But, according to the new hypothesis, we have further examples of molecular compounds in phosphorus chloride, PCl_5, and in ammonium chloride, NH_4Cl. In the former, a molecule of PCl_3, a true atomic compound, holds in combination a molecule of chlorine Cl_2, also an atomic compound. In the latter, a molecule of NH_3, an atomic compound, holds in combination a molecule of hydrochloric acid, also an atomic compound.

Foundation for the Distinction between Atomic and Molecular Compounds.—Of course, in order that such an hypothesis as that under consideration should be at all permissible, it must be shown that there are differences between those compounds which are called molecular, and those which are called atomic. To a certain extent this has been supposed to be possible. In the case of salts containing water of crystallization, there is, at least generally, no difficulty in recognizing that the force holding together the salt and the water is not as strong as that which holds the constituents of the salt together, or that which holds the constituents of the water together. It is only necessary to heat the compounds gently in order to overcome the attraction and cause the breaking up of the complex molecule; in some cases, indeed, the attraction is so weak that it is only necessary to expose the compound to the air, when the water passes off in the form of vapor, leaving the molecules of the salt intact. This weakness of union is then regarded as a principal characteristic of molecular combination.

Now, if the compounds above referred to, viz., PCl_5 and NH_4Cl, be examined, it will be found that they possess this characteristic. It has been shown, when considering the cases of anomalous specific gravities of vapor, that when phosphorus pentachloride, PCl_5, and ammonium chloride, NH_4Cl, are heated to a sufficient degree to convert them into vapor, they are broken up into the trichloride, PCl_3, and chlorine, Cl_2, and ammonia, NH_3, and hydrochloric acid, HCl, just as the crystallized salts lose their water of crystallization by being heated. So, also, in a number of other cases, it can be shown to be true that compounds, which must be considered as molecular in order to explain their existence and yet retain their hypothesis of constant valency, as above stated, break down under the influence of heat into simpler molecules.

It will thus be seen that there is some foundation for assuming the existence of molecular compounds as distinct from atomic compounds. But how does this help us?

Use of the Distinction.—It is plain that atomic compounds are the only ones which we can employ for the purpose of determining the valency of atoms. Thus, the only chlorine compound of phosphorus that can be employed for the purpose of determining the valency of phosphorus is the trichloride. The other compound, PCl_5, the existence of which would seem to indicate that phosphorus is quinquivalent as well as trivalent, being according to the new hypothesis a molecular compound, is formed independently of the valency of phosphorus and does not at all interfere with the acceptance of the view that valency is a constant property. So, too, in all similar cases. Nitrogen is really trivalent, but, owing to the formation of molecular compounds, it appears oftentimes to be quinquivalent. By a generous application of this hypothesis, there is no difficulty in accounting for the anomalous cases, and the hypothesis of valency may still be retained, unless it can be shown that there are facts, not yet considered, which do not harmonize with it.

Difficulties met with.—One difficulty immediately presents itself. Although the examples above given show that there are compounds which seem to differ from true chemical compounds to a sufficient extent to justify the assumption

that they belong to another class of compounds, still there are cases in which there is no ground whatever for making this assumption, and which, nevertheless, show plainly that one and the same element may be at one time trivalent, at another quinquivalent, unless the above assumption be made without any experimental basis whatever. The compound, $POCl_3$, *for instance, is not decomposed when converted into vapor*, and we have just as much right to consider it a true chemical compound as we have to consider the trichloride, PCl_3, as such. But in the oxychloride, $P\overset{II}{O}\overset{III}{Cl_3}$, phosphorus is apparently quinquivalent, while in the trichloride, PCl_3, it is trivalent. Evidently, here the only ground for considering the oxychloride, $POCl_3$, a molecular compound is the fact that its existence cannot be explained by the hypothesis of constant valency, unless indeed we conceive it to be represented by the formula $P\begin{matrix}\diagup OCl \\ —Cl \\ \diagdown Cl\end{matrix}$, as some have done. This is dangerous reasoning, and, if we follow it, we shall soon be in serious difficulties. It was seen above that ammonium salts can be explained only on the supposition that the nitrogen in them is quinquivalent, unless they are assumed to be molecular compounds. Plainly, it would be next to absurd to make this supposition, as they have all the characteristics of true chemical compounds, and if it can be assumed that they are only molecular compounds, in order to suit our purpose, then we are at liberty to make the same assumption in regard to almost any compound in the field of chemistry.

Further, the fact that a compound is easily decomposed by heat or by any other means is very weak evidence in favor of the view that it is molecular, for, as is well known, there are many compounds which must be regarded as true chemical compounds, and which are, nevertheless, extremely unstable.

Experiments showing that Nitrogen may be both Trivalent and Quinquivalent.—Again, an experiment has been performed which appears to show that ammonium chloride, NH_4Cl, and analogous compounds of nitrogen, are true atomic compounds. If ammonium chloride, NH_4Cl, be a

molecular compound, then, as was explained above, two forces are concerned in the formation of its molecule.

1st. A force holding together the nitrogen atom and three hydrogen atoms forming the molecule NH_3; and the hydrogen atom and chlorine atom forming the molecule HCl.

2d. A force holding together the molecule NH_3 and the molecule HCl.

If these two forces are distinct in character, the resulting molecule may be represented by the formula (NH_3+HCl). Suppose now we add together two other molecules, such that, taken together, their constituent atoms are the same in number and quantity as those contained in the compound (NH_3+HCl). Then the resulting compound ought not to be identical with that obtained in the former case. If these new molecules are, for instance, NH_2Cl and H_2, then the compound will be (NH_2Cl+HH), and this should not be identical with (NH_3+HCl), although its composition is exactly the same.

This method of investigation has been applied to the study of the problem under consideration, not, indeed, with the molecules employed in the above explanation, but with others analogous to them. Instead of ammonia, NH_3, the analogous compound, $N(CH_3)_3$, was taken, and this was united with ethyl iodide, C_2H_5I. Thus, a compound was obtained which, if it be molecular, should be represented by the formula $(N(CH_3)_3+C_2H_5I)$. Again, the compound, $N(CH_3)_2C_2H_5$, was taken, and this was united with methyl iodide, CH_3I, yielding a compound which should be represented by the formula $(N(CH_3)_2C_2H_5+(CH_3)I)$. Now these two new compounds ought not to be identical, if they are molecular and not atomic. On comparing them, however, they were found to be in every respect identical.

From this experiment it is concluded that the compounds studied are atomic compounds, and that in them nitrogen is quinquivalent. Each group (CH_3), (C_2H_5), and the element, I, being held by the same kind of force, the identity of the resulting compounds is readily understood.

As was stated in a previous chapter, the compound, PCl_5, can be converted into vapor under certain circumstances, viz., in the presence of the vapor of the trichloride, PCl_3. From this it is concluded that the compound, PCl_5, is a true chemical or atomic compound; and, hence, further, that the phosphorus atom contained in it is quinquivalent.

The Distinction between Atomic and molecular Compounds unnecessary as far as the Hypothesis of Valency is concerned.—It appears, therefore, that nitrogen and phosphorus act in some compounds as trivalent, in other compounds as quinquivalent, elements. If this be acknowledged, however, then there is no necessity for assuming the existence of molecular compounds for the purpose of explaining anomalies in the valency of elements. It is possible that in some of the so-called double compounds, in which two or more salts appear to be combined with each other, as well as in the salts containing water of crystallization, we have examples of true molecular compounds, in the sense in which this expression has been used in the present article; but it is evident that, as soon as the possibility of one and the same element being either univalent or bivalent is admitted, it is no longer necessary to assume the existence of these molecular compounds. At present the hypothesis of molecular compounds does not play an important part in dealing with the phenomena of valency. It seems not improbable that when the subject of valency is thoroughly understood it will be found competent to explain all compounds that are made up of constituents combined in definite proportions.

Saturated and Unsaturated Compounds.—As soon as the quinquivalence of nitrogen was established, a new explanation was offered concerning the nature of nitrogen compounds. Only those compounds in which the nitrogen is quinquivalent were looked upon as complete. Those in which the nitrogen is trivalent were looked upon as incomplete. For the expressions complete and incomplete, the expressions saturated and unsaturated were employed. The atom of nitrogen having the power to hold in combination five univalent elements or groups is *saturated* when all of its powers are employed, as in the compound NH_4Cl; it is *unsaturated* when only a part of its powers are employed, as in the compound NH_3. The power of the nitrogen atom was expressed by saying that it possesses five *affinities* or *bonds*. In the saturated compound all of these affinities are employed, whereas in the unsaturated compound only a part of them are employed.

Maximum Valency and Apparent Valency.—According to the hypothesis of saturated and unsaturated com-

pounds, then, each element is conceived to have a certain maximum valency towards each other element. But an element may not always exert its maximum valency, and may appear to have a lower valency than the maximum. The maximum valency of phosphorus towards chlorine is that shown in the pentachloride. In the trichloride its apparent valency is three; nevertheless, the phosphorus is quinquivalent towards chlorine, as is shown by bringing chlorine in contact with the unsaturated compound, when it becomes saturated to form the pentachloride. So also carbon is regarded as quadrivalent towards oxygen, but its apparent valency in carbon monoxide, CO, is two.

Maximum Valency is dependent upon Conditions.—As regards the maximum valency of an element no absolute statement can be made. When the statement is made that phosphorus is quinquivalent, the words, at the ordinary temperature, must be added if we are to confine our statement to what we know. It has already been shown that at elevated temperatures phosphorus pentachloride is decomposed into the trichloride and chlorine. Thus it is clear that at this elevated temperature phosphorus is trivalent towards chlorine. So, too, while nitrogen is quinquivalent at the ordinary temperature towards hydrogen and chlorine together, it becomes trivalent at a higher temperature. In general, the complexity of compounds becomes less and less as their temperature is elevated more and more; or, in other words, *the valency of the elements decreases with increase of temperature.*

Are all the Bonds of an Element of the same order?—This question is suggested by the easy decomposition of such compounds as phosphorus pentachloride, ammonium chloride, etc., when heated. To account for the facts it has been assumed that of the five bonds or affinities of the nitrogen atom and of the phosphorus atom two are weaker than the other three. Hence, in a saturated nitrogen compound two atoms or groups have been supposed to be held less firmly in combination than the other three, and they are given off more readily. The experiment described above, however, which proved the identity of the compounds [$N(CH_3)_3 + C_2H_5I$] and [$N(CH_3)_2(C_2H_5) + CH_3I$], also appears to show that the affinities of the nitrogen atom are all of the same kind, and hence it cannot be ad-

mitted that two of the affinities are weaker than the other three. While, further, phosphorus pentachloride, PCl_5, is readily decomposed by heat, in accordance with the supposition that two of the affinities of the phosphorus atom are weaker than the other three, yet, on the other hand, the *compound, $POCl_3$, gives no evidence of this difference of* the affinities. It can also easily be shown that it is not necessary to assume this difference in order to explain the decomposition of phosphorus pentachloride, PCl_5, and ammonium chloride, NH_4Cl. It may, for instance, be supposed that the five affinities of the nitrogen atom, or the phosphorus atom, are all exactly equal in power at the outset. Should three of these affinities, however, become saturated, it seems possible that the presence of the saturating atoms or groups may influence the power of the remaining unsaturated affinities in such a way as to make them weaker than they were at first; or it may be assumed that in the saturated compound each atom of chlorine is held by the phosphorus atom with exactly the same force, but that this force is less than that exerted between the phosphorus and each atom of chlorine in the trichloride.

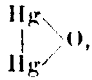
It seems rational to suppose that, in phosphorus trichloride, for example, all three of the chlorine atoms are influenced in exactly the same way by the phosphorus, and that the whole atom of phosphorus is brought into play. Further, that under certain circumstances the same power of the phosphorus may be distributed uniformly among five chlorine atoms, but that then the compound is less stable than the simpler one. On heating the less stable compound it loses two chlorine atoms, and the more stable one is formed.

Self-saturation of Atoms.—To account for the existence of unsaturated compounds it has been suggested that two affinities of the same atom might in some way act upon each other, causing saturation. The compound in which such a combination exists is then a complete compound, not possessing free affinities. In such compounds, however, the mutual saturation of like affinities can easily be overcome, and then other atoms can be held in combination. This explanation appears probable in the light of the fact that the number of latent affinities in unsaturated compounds is always, with very few exceptions, an even

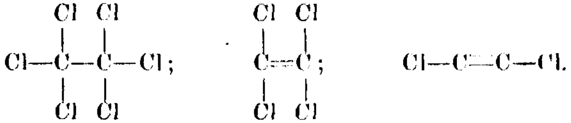
number. This would necessarily be the case if the above assumption were true. There are, however, undoubted exceptions to this rule, among the most marked being nitric oxide, NO, and tungsten pentachloride, WCl_5, tungsten having a maximum valency of six towards chlorine. On the other hand, phosphorus and nitrogen are trivalent or quinquivalent, sulphur bivalent, quadrivalent, or sexivalent, the halogens univalent, trivalent, quinquivalent, or septivalent. Notwithstanding the exceptions, this rule of change is suggestive and needs explanation.

Single, Double, and Triple Linkage of Atoms of the same Kind.—Another explanation of apparent variations in valency applicable to a number of cases is that atoms of the same kind may partly saturate each other, somewhat as they are supposed wholly to saturate each other in the molecules of polyvalent elements. For example, the molecule of oxygen is regarded as made up of two bivalent atoms, and is represented by the symbol O=O. Here the atoms are regarded as united by double linkage, a condition of things which is also believed to exist in such compounds as the oxides of calcium, magnesium, etc., Ca=O, Mg=O. If, however, these atoms be regarded as united by single linkage as oxygen and hydrogen are united in water H—O—H, then the double atom of oxygen, instead of being saturated, will itself be bivalent, as it is supposed to be in hydrogen peroxide H—O—O—H. This explanation is commonly accepted for the compounds of copper and mercury. These elements are bivalent, as shown by the compounds $CuCl_2$, $HgCl_2$, CuO, HgO, etc. Nevertheless, as is well known, in the so-called cuprous and mercurous compounds they are apparently univalent. It is suggested, however, that in these latter compounds a condition of things exists like that above referred to as probably existing in hydrogen peroxide. If in the cuprous *compounds two copper atoms are in combination by one* bond, the double atom is bivalent or the single atom would appear to be univalent, and the same remark applies to the mercurous compounds. This view is expressed in the formulas:—

Cl—Cu—Cu—Cl, cuprous chloride; $\begin{matrix}\text{Cu}\\|\\\text{Cu}\end{matrix}\!\!>\!\text{O}$, cuprous

oxide; Cl—Hg—Hg—Cl, mercurous chloride;  mercurous oxide.

But just as atoms of the same kind must in many cases be regarded as held in combination by single linkage, so too, in many cases, the assumption that atoms of the same kind are united by double or by triple linkage, affords a simple explanation of variations in valency. Examples are furnished by the three chlorides of carbon, C_2Cl_6, C_2Cl_4, and C_2Cl_2, and the three hydrocarbons C_2H_6, C_2H_4, and C_2H_2. In all these, carbon is regarded as quadrivalent, but, while in the chloride C_2Cl_6 the carbon atoms are believed to be united in the simplest way called single linkage, in the chloride, C_2Cl_4, they are believed to be united by double linkage, and in the chloride, C_2Cl_2, by triple linkage. These ideas are expressed in the formulas—



If the question be asked what is meant by these double and triple lines, it can only be answered that they are intended to express the idea that in the case of the doubly linked atoms the condition of single linkage is probably repeated twice, and that in the case of triply linked atoms this condition is repeated three times. In regard to the nature of single linkage itself we have no clear conception. As regards experimental evidence in favor of these views it must be acknowledged that there is very little, and that is furnished by a study of the compounds of carbon. It will be presented when these compounds are taken up.

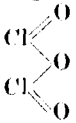
It will be noticed that the above method of explaining apparent variations in the valency of double atoms implies that these variations take place by pairs. That is to say, the valency of a double atom may, according to this, be two, four, six, eight, etc., but such a double atom would never have a valency of one, three, five, etc. A similar explanation can be offered for cases in which groups of atoms have a valency of one, three, five, etc., but cases of this kind are not known, and the explanation is therefore

superfluous. This change of valency by pairs in the case of groups of atoms suggests that possibly some similar cause may operate in the case of the variations in valency of what we call single atoms. The connection existing between the properties of the elements and their atomic weights, which is clearly recognized in the periodic law, suggests that what we call elements are in reality not elements, but compounds of the true elements. If this be true, and probably very few doubt it, then it follows that what we call atoms are not atoms, but groups of atoms. The change in the valency may possibly be due to changes in the relations of the atomicules of which the atoms themselves may be made up. It must be acknowledged that at present there is no evidence in favor of this view. It is simply an interesting speculation.

Relative Valency.—It will be clear from what has been said that the variations in valency are not always supposed to be due to the same cause. That it varies with the temperature cannot be questioned. Why, we do not know. Again, that it apparently varies in consequence of the union of atoms of the same kind in different ways is a very plausible hypothesis, which satisfactorily explains a number of cases. The suggestion that some compounds are saturated and others unsaturated is in itself not an attempt at an explanation, but is merely a restatement of the fact that demands explanation. There is no well-established hypothesis to account for those cases in which the valency of an atom varies with reference to some other atom, as in the case of phosphorus and chlorine, carbon and oxygen, etc. The suggestion that atoms consist of groups of atomicules, if it could be shown to be well founded, would bring the cases referred to within the applications of the hypothesis made use of to account for variations in the valency of groups of atoms. In the early part of this chapter it was pointed out that the valency of an element varies according to the character of the elements with which it combines. In other words, valency is a relative property. The valency of an element may be constant towards some elements and variable towards others. Thus, the valency of the members of the chlorine family towards hydrogen and towards most of the so-called metals is constant, while towards oxygen, and towards hydrogen and oxygen together, it apparently

varies between one and seven. The valency of sulphur towards hydrogen is constant, but towards oxygen, and towards hydrogen and oxygen, it varies from four to six, and towards chlorine from two to four.

At present no satisfactory explanation can be offered for the fact that valency is relative. It is clear that the hypothesis adopted to account for variations in valency towards one and the same element will not explain why sulphur should be bivalent towards hydrogen and sexivalent towards oxygen. It is true a similar hypothesis has been put forward to explain some cases of apparently variable valency. Thus, it has been suggested and long taught that chlorine is univalent towards oxygen as well as towards hydrogen, and that in the oxides and oxygen acids of chlorine the atoms of oxygen are combined in what are called chains. Thus, instead of assuming that chlorine is trivalent in the compound Cl_2O_3 or



it was assumed to be univalent and the compound represented thus, Cl—O—O—O—Cl. The only reason for this was that valency was regarded as necessarily constant; and, as it is unquestionably univalent in hydrochloric acid, it must, therefore, be univalent in all other compounds. In the same way perchloric acid was considered as made up as represented in the formula Cl—O—O—O—O—H. The chief objection to this view is that it is founded upon the hypothesis of constant valency, which is not tenable. Another objection to it is that, so far as can be determined, compounds in which oxygen atoms are linked together are characterized by great instability, as is shown in hydrogen peroxide, while the chlorates and perchlorates are relatively stable substances, and the stability of the oxygen compounds of chlorine is greater the greater the quantity of oxygen in them. It will also be shown further on that many compounds of iodine can be understood only on the supposition that they contain septivalent iodine, and that all the oxygen acids of the halogens are easily explained on the supposition that in them the halogens are either univalent, trivalent, quinquivalent, or septivalent.

Periodic Variations in Valency.—The valency of the elements acquires additional interest when examined in the light of the periodic law. It will be seen that the valency varies with the position of the elements in the periodic system. This is shown to some extent in the tables on pages 83, 84, and 86. Referring to that on page 83 it appears that from Group I. to Group VIII. there is a regular increase in the proportion of oxygen contained in the oxides represented by the formulas—

R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8
	(RO)		(RO_2)		(RO_3)		(RO_4)

As has already been pointed out, it is possible that in some of these oxides oxygen may be linked to oxygen, in which case the oxygen valency would not be as great as appears from the formula. Considering, on the other hand, the regularity of the increase from one end of the series to the other, the view that this regular increase in complexity is due to increased valency for oxygen appears to be the most rational. It may be said in general, then, that the oxygen valency of the elements increases regularly from one to eight from Group I. to Group VIII. The members of Groups I. to III. cannot be spoken of as having any hydrogen valency, or, perhaps better, our knowledge of the hydrogen compounds of these elements is so imperfect that no definite statement can be made concerning the hydrogen valency. Beginning with Group IV. the highest hydrogen valency is exhibited, and from this to Group VII. there is a regular decrease in the hydrogen valency from four to one. Further, the valency of an element towards hydrogen is constant.

Similar regularities are observed in the chlorine valency, which, like the oxygen valency, varies in one and the same element. The maximum chlorine valency is six, as in the compound tungsten hexachloride WCl_6. There is a regular increase in the chlorine valency from one in Group I. to six in some members of Group VI., and then a falling off when Group VII. is reached. There are, further, some irregularities presented by the chlorides which need explanation, as, for example, the easy transformation of tungsten hexachloride into the pentachloride. Another peculiarity met with among the chlorine compounds is that some of the members of Group III., as, for example, aluminium, form

chlorides of the formula M_2Cl_6, according to which they appear to be quadrivalent, while their position in the system and the composition of many of their compounds indicate that they are trivalent. As regards these cases, however, it has been suggested that in them the chlorine may be the linking element. If it be assumed that a double chlorine atom (Cl_2) can take the place of one oxygen atom, then not only the compounds, like Al_2Cl_6, but all the so-called double chlorides can be easily explained. This view has been fully discussed in articles by the author of this book.*

The hydroxides can all be explained most readily by assuming that the valency of the elements towards oxygen and hydroxyl (OH) increases regularly from one to seven from Group I. to Group VII. It will be shown further upon what grounds the hydroxides are regarded as containing the univalent group hydroxyl (—O—H). The univalent metals form hydroxides of the general formula M(OH), the bivalent metals form hydroxides of the general formula $M(OH)_2$, etc. Now, if the table of hydroxides on p. 81 be examined, it will be seen that up to Group IV. there is a regular increase in the number of hydroxyl groups held in combination. The hydroxides of Group IV. show a marked tendency to give up the elements of water, and thus to form compounds with a smaller number of hydroxyls. Thus the hydroxide of carbon corresponding to the maximum oxygen valency would have the formula $C(OH)_4$; but this compound cannot exist. It loses water and passes back to the form $CO(OH)_2$, and even this is extremely unstable, breaking down at the slightest elevation of temperature into water and carbon dioxide. The maximum hydroxide of silicon can be prepared, but it changes to the acid $SiO(OH)_2$, and this further to SiO_2, though these changes take place much less readily than in the case of carbon. The simplest interpretation of the changes referred to is that the valency of the elements is not changed. Representing the maximum

* See American Chemical Journal, Vols. XI., XIV.

hydroxide of silicon by Si $\left\{\begin{array}{l}OH\\OH\\OH\\OH\end{array}\right.$ or $Si\begin{array}{l}\diagup OH\\ \lt OH\\ \lt OH\\ \diagdown OH\end{array}$, the simplest view is that, when it loses a molecule of water, it becomes $Si\begin{array}{l}\diagup\!\!\diagup O\\ —O—H\\ \diagdown O—H\end{array}$, in which the silicon is still quadrivalent. In the same way the maximum hydroxides of Group V. would have the formula $M(OH)_5$, but these do not exist. They lose water and form compounds of the general formulas $MO(OH)_3$ or $MO_2(OH)$, as, for example, phosphoric acid, $PO(OH)_3$ and nitric acid $NO_2(OH)$. But, just as the oxygen valency of the members is variable, being in some compounds three and in others five, so, too, the hydroxyl valency varies. There are compounds, for example, derived from the hydroxides $M(OH)_3$. Phosphorous acid appears to be the phosphorus compound of this formula; and nitrous acid is derived from the hydroxide $N(OH)_3$ by loss of water, much in the same way that nitric acid is derived from the hydroxide $N(OH)_5$. It is accordingly represented by the formula $NO(OH)$.

In Group VII. the maximum hydroxides have the general formula $M(OH)_6$, but these generally break down by the loss of two molecules of water, forming compounds $MO_2(OH)_2$, of which sulphuric acid $SO_2(OH)_2$ and chromic acid $CrO_2(OH)_2$ are examples. In these compounds the sulphur and chromium are regarded as sexivalent, and this view is thus expressed: $\begin{array}{l}O\\O\end{array}\!\!\gg\! S \!\begin{array}{l}\diagup O—H\\ \diagdown O—H\end{array}$ and $\begin{array}{l}O\\O\end{array}\!\!\gg\! Cr \!\begin{array}{l}\diagup O—H\\ \diagdown O—H\end{array}$.
Sulphurous acid and similar acids are regarded as derived in the same way from quadrivalent hydroxides $M(OH)_4$. Thus sulphurous acid is represented by the formula $SO(OH)_2$.

In Group VII., finally, the maximum hydroxides have the formula $M(OH)_7$, but these generally break down to the form $MO_3(OH)$ or $M\begin{array}{l}\diagup\!\!\diagup O\\ \diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\\ \diagdown O—H\end{array}$; examples are perchlo-

ric and periodic acids. Other compounds are derived from the hydroxides $M(OH)_5$, $M(OH)_3$, and $M(OH)$. The first two, like the hydroxide $M(OH)_7$, break down to a hydroxide containing but one hydroxyl. Examples are chloric acid $ClO_2(OH)$ and chlorous acid $ClO(OH)$. Thus it will be observed that the maximum hydroxides of the members of Groups V., VI., and VII. do not exist, or are very unstable compounds, but that they break down by loss of water *generally forming compounds in which the number of hydroxyl groups corresponds to the hydrogen valency of the members of the group.*

Finally, the valency of an element is greater towards similar elements than towards those of a different kind. This is shown most strikingly in the case of the members of Group VII. Towards oxygen, which they resemble in many respects, their valency is high; towards hydrogen and the alkali metals the valency is low. The same is true, though in a less marked way, of the members of Groups VI. and V., while the members of Group IV. have the same valency towards hydrogen, oxygen, and chlorine.

Classification of the Elements with Reference to their Valency.—As the valency of the elements varies in many cases both towards one and the same element, and towards different elements, it is plain that any attempt to classify the elements according to the valency, except in some very broad way, must be unsuccessful. Nor is there much, if any, value in such attempts at present. We must first learn more about the laws governing the variations, and we shall acquire the desired knowledge not by assuming that because an element has a certain valency in one compound it must therefore have it in all others, and then turning and twisting all the facts so as to avoid giving up this unwarranted assumption; but by determining independently in as many cases as possible what valency the elements actually exhibit, and then seeing what general conclusions can be drawn.

Application of the Views concerning Valency to the Study of Chemical Compounds.—Up to the present the chief value of the views concerning valency has been in connection with the study of the constitution of the compounds of carbon, and particularly for the purpose of expressing the relations between carbon, oxygen, and hy-

drogen. The application to the study of the constitution of the so-called inorganic compounds has not been as successful, mainly for the reason that these compounds do not undergo transformations as readily as those of carbon, and therefore not as much is known about them. On the other hand, the constitution of most of the familar inorganic compounds is comparatively simple, and the determination of their constitution is also comparatively simple.

CHAPTER VIII.

CONSTITUTION OR STRUCTURE OF CHEMICAL COMPOUNDS.

DEFINITION OF CONSTITUTION, ETC.

Definition, etc.—If all chemical compounds could be converted into vapor without suffering decomposition, and the truth of Avogadro's hypothesis could be established beyond reasonable doubt, it would be possible to determine the molecular formulas of these compounds. The steps involved in determining the formula of a compound are these:—

1. The compound must be analyzed; the percentages of its constituents must be determined. This involves no hypothesis. If, in expressing the results of the analysis, we say the compound contains a certain percentage of carbon, a certain percentage of oxygen, and a certain percentage of hydrogen, we simply state facts.

2. If, however, we express the results by a chemical formula we then make use of some hypothesis. At the present day the hypotheses involved in the simplest chemical formulas, such as HCl, H_2O, H_3N, etc, are (1) the atomic hypothesis, and (2) Avogadro's hypothesis. In writing these formulas we mean to express the composition of a molecule of each compound. In many cases the molecular weight cannot be determined. Thus, take sodium sulphate. We write the formula Na_2SO_4 for the compound, but we have no means of judging whether this formula expresses the true molecular weight of the compound or not. It expresses the percentage composition, and, if we accept the atomic weights as determined by the rules of Avogadro and of Dulong and Petit, the formula given is the simplest one possible. This is the only reason for adopting it. As far as experimental evidence is concerned, the formulas $Na_4S_2O_8$ or $Na_6S_3O_{12}$ are fully as satisfactory, and, indeed, there are some facts known which seem to indicate that these more

complex formulas are really nearer the truth than the simple one now in use. This, however, is not a matter of much importance in the present stage of chemistry. For most purposes the formula Na_2SO_4 is quite satisfactory.

The formulas which simply express the percentage composition of molecules are commonly called *empirical formulas*. Can anything else be fairly represented by a chemical formula? It will be observed that the empirical formulas have nothing whatever to do with the conduct of the compounds they represent. On studying the action of chemical compounds upon one another we gain a mass of knowledge which it is very desirable to express in a concise form. We find that certain compounds resemble one another very closely in their conduct, though they may differ markedly in composition; we learn that the presence of certain constituents in a compound causes it to act in a particular way; we learn that, although the number of compounds is unlimited, the number of classes of compounds is comparatively small, etc. etc. If formulas can be devised which will aid us in expressing intelligibly the results of investigation, they must be of value.

From the earliest periods of chemistry formulas of this kind have been used. Without going back to the beginning it will be instructive to recall the general character of these formulas from the time of Lavoisier.

This chemist, as is well known, paid particular attention to the phenomena of combustion. He regarded all compounds as made up of a combustible and incombustible part. In his formulas he separated these two parts.

When the electro-chemical theory held sway every compound was supposed to consist of an electro-positive and an electro-negative constituent. Hence, every formula consisted of two parts. To determine the formula according to this theory, a compound was subjected to the decomposing influence of the electric current. It was thus separated into two parts, and these parts were written separately in the formula. The old formulas for salts, such as $NaO.SO_3$, $KO.NO_5$, etc., which we see even at the present day, particularly in works on mineralogy and analytical chemistry, have come down to us from the period of the electro-chemical theory. They involve more speculation than the formulas now in use, and that, too, of a kind which has been shown to be unfounded.

The next idea which we find playing an important part in the construction of chemical formulas is that used by Liebig. This chemist, and many others after him, effected the decomposition of compounds and noticed what products were obtained. In writing the formula of the original compound, they indicated in it the presence of the products they had obtained from it.

After this came the idea of types, which was developed by Dumas and became known as the "theory of types." According to this "theory" all chemical compounds may be referred to a few fundamental compounds or types. All compounds belonging to the same type are constructed on the same plan. The types which have been proposed up to the present time are:—

I.	II.	III.	IV.
HCl,	H_2O,	H_3N,	H_4C.
Hydrochloric Acid.	*Water.*	*Ammonia.*	*Marsh-Gas.*

There is something distinctive in each of these compounds, and the traits which characterize it are met with in the compounds belonging to the same type. On attempting to make use of the type theory for the purpose of classifying compounds serious difficulties are met with, mainly for the reason that many compounds belong, not to one type, but to several.

The introduction of the idea of "mixed types" did much to overcome these difficulties, but still, without extension, the idea of types could not furnish a sufficient basis for formulas which should express the principal facts known regarding chemical compounds. The "theory" was, however, of great importance, as it furnished a rational means of classifying chemical compounds, and directed attention to fundamental differences between the elements.

An examination of the types shows that the elements chlorine, oxygen, nitrogen, and carbon differ from one another in their power of holding hydrogen in combination, and leads to the conclusion that the reason for the existence of these types must be looked for in the nature of the elements of which they are composed. This brings us at once to the valency hypothesis, which has already been discussed. At the present time chemical formulas are based upon the atomic hypothesis, the hypothesis of Avogadro, and the valency hypothesis. As there is a

great deal of misunderstanding in regard to these formulas, as by some they are overvalued, and by others undervalued, a brief statement concerning their exact significance is desirable.

It cannot be denied that we are now in a period of chemistry which may fairly be called one of *formula worship*. More value is sometimes attached to a formula than to that which it is intended to represent. In consequence of this it has happened that a large number of chemists have regarded the determination of a formula for a compound as the great object to be accomplished, and they have forgotten that what we ought to know, and what is of vastly greater importance for the science, is the chemical conduct of the compound. If, knowing this, we can represent it by means of a formula, not only are we justified in doing so, but the formula becomes an efficient aid in dealing with the compound. Formulas have been proposed for nearly all compounds known. Some of these, indeed many of them, are valuable, but many are not. Before considering the means at our command for deciding whether a formula is valuable or not, a few words in regard to the general methods in use for determining formulas will be necessary.

After the empirical formula, as above defined, has been determined, the next thing to be done is to study the compound in every possible way, both by chemical and physical methods. We must learn exactly how it conducts itself under all circumstances which we can control. When this study is finished we shall have in our possession a mass of facts. We shall know much more than the composition, and we ought to be able to express much more than the composition by our formula. It is, however, by no means necessary that these facts should be expressed in the formula, any more than it is necessary that the composition should be expressed in a formula. Now, how can we express anything in regard to the conduct of a compound by means of a formula? As a simple example, acetic acid may be taken. The empirical formula is easily found to be $C_2H_4O_2$. We find that exactly one-fourth of the hydrogen contained in the compound can easily be replaced by metals. Thus, with potassium hydroxide or carbonate we get $C_2H_3O_2K$. We cannot replace any more of the hydrogen by metals, so that we are justified in concluding

that one of the four parts of hydrogen, represented in the empirical formula, differs from the other three. We may, hence, write the formula $C_2H_3O_2.H$, which expresses the difference found by experiment.

Further, when acetic acid is treated with phosphorus trichloride, it is converted into a compound of the formula $C_2H_3O.Cl$; that is, the acid loses one atom of hydrogen and one atom of oxygen, and takes up in place of them one atom of chlorine. When the chlorine compound is treated with water, acetic acid is regenerated, and hydrochloric acid is formed:—

$$C_2H_3O.Cl + H_2O = C_2H_3O_2.H + HCl.$$

This reaction makes it appear probable that, in acetic acid, one of the oxygen atoms is intimately associated with a hydrogen atom. The two leave the acid together, and enter it together. We may express this fact by the formula $C_2H_3O.OH$. The chlorine compound, formed by treatment with phosphorus trichloride, contains no hydrogen replaceable by metals, so that it appears extremely probable that the hydrogen, which is represented by itself in the formula $C_2H_3O_2.H$, is the same as that represented as associated with oxygen in the formula $C_2H_3O.OH$. In a similar way it can be shown that the second oxygen is probably associated with carbon in the same way as it is in carbon monoxide. We, hence, write $CO.CH_3.OH$. This formula expresses the result of reactions studied, and it may, hence, be called a *reaction formula*. We can supplement the knowledge gained by the reactions above referred to by making acetic acid from simpler substances, that is, by the process of synthesis. Thus, for example, we may start with marsh-gas, CH_4, and carbonyl chloride, $COCl_2$. These substances, or similar substances, act upon each other as represented thus:—

$$CH_4 + COCl_2 = CH_3.COCl + HCl.$$

If the product $CH_3.COCl$ is found to be identical with that above mentioned as resulting from the action of phosphorus trichloride on acetic acid, and which was represented by the formula $C_2H_3O.Cl$, then, taking into consideration the facts above mentioned, we are led to the formula $CH_3.CO.OH$ for acetic acid. This formula, as far as it is based upon the synthesis of acetic acid, may be called a *synthesis formula*.

together, that there is some definite arrangement between them.

Having been led to this view, the problem presents itself in the case of every compound to determine how the atoms are linked together. If we can do this we can determine the constitution of the compound, and, if the determination is properly made, the result is almost entirely independent of the hypothesis of valency. As already pointed out, we can determine these relations only by means of experiment. The determination is never absolute. All that we can say is, that the compound conducts itself *as if* hydrogen and oxygen were united, or *as if* two carbon atoms were linked together, and we then make use of a formula to recall this to mind. Such relations, established by actual experiment, are about all we can express in the formula, and, if we then go beyond them, and distribute the "bonds" so that all are satisfied, we are dealing with pure hypothesis, and are not gaining any additional insight into the nature of the compound.

If the question be asked, What is the meaning of the expression "linkage of atoms?" the only answer that can be properly given is, that it is simply a convenient phrase to indicate the condition which we believe to exist between the smallest parts of all chemical compounds. As to its character we know absolutely nothing. If we could tell exactly what relation the smallest particle of chlorine bears to that of hydrogen in hydrochloric acid, we could tell what is meant by "linkage of atoms." All that we know is that the chlorine and hydrogen do act upon each other in some wonderful way, that they both disappear as such, and that we get something in which both are present. We believe that the act of union takes place between the atoms of the elements, and we represent the compound by the formula HCl, or H.Cl, or H—Cl. It is not at all probable that a firm union exists between the two parts in such a way as to render the parts of the molecule immovable with reference to each other. Much more likely is it that, after the union, the atoms perform some kind of motion with reference to each other, according to the laws of atomic motion yet to be discovered. For our present purpose it is sufficient to know that, in whatever manner the union takes place, the chemical activity of the atoms is differently occupied in consequence.

In writing a structural formula, we do not commit ourselves in regard to the character of the union between the parts, nor, generally, in regard to the position of the parts in space. *All that we can attempt to do at present is to indicate* the probable relation between the parts. Thus, by the formula, $H_3C—C—N$, we mean that the reactions and *methods of formation of the compound represented lead* to the conclusion that the two carbon atoms are closely related or linked together, while the three hydrogen atoms are linked to one of the carbon atoms and the nitrogen to the other. The reactions of the substance and the methods of formation lead us to believe that these relations exist in it. If we go farther and represent the substance by the formula $H_3C—C\equiv N$, we are then simply applying the hypothesis of valency, and we gain little if anything. We know practically nothing about the relation existing *between the carbon and nitrogen, though the above formula* seems to indicate that the relation is a firmer one than that expressed by the simple line as $C—N$.

The formulas in use for the various classes of compounds known to us will now be considered, more particularly with the object of showing the connection existing between the facts and the formulas. After the classes have been discussed, the principal compounds of each class will be taken up and treated in a similar manner. In this section the proofs made use of will be entirely of a chemical character. In a subsequent *section the question of the relations* between physical properties and constitution will be briefly discussed.

CHAPTER IX.

CONSTITUTION OF CLASSES OF COMPOUNDS.

CHEMICAL compounds may be most conveniently classified according to their chemical properties. No system of classification which has been proposed up to the present can, in any sense, be called perfect, and yet the system in common use is convenient, and has a fair foundation of facts.

The compound which has the formula HCl, hydrochloric acid, and the compound which has the formula KOH, potassium hydroxide, differ very markedly from each other. The former has a taste which we call sour, the latter has the taste of lye, or an alkaline taste. The former will turn the color of many organic substances, while the latter will undo the work done by the former, restoring the original color. In whatever way we may consider these two compounds, we shall find that they have opposite or complementary properties. They are both chemically active substances, capable of producing marked changes in large numbers of other compounds. If they are brought together they neutralize each other; that is to say, they destroy each other's characteristic properties, and give rise to the formation of a new compound, differing entirely from the two. The two compounds, hydrochloric acid, HCl, and potassium hydroxide, KOH, are representatives of two great classes of compounds known as *acids* and *bases*. Many of the members of these two classes possess just as marked properties as do the two which have been mentioned, and for these the classification into acids and bases is rational and simple. But there are, further, some compounds which appear to possess the characteristics of both classes to a certain extent, and of neither class very markedly. They act like acids towards some bases, and like bases towards some acids. The way they act depends upon the character of the substances with which they are brought in contact.

Acids.—The properties which characterize acids are the following:—

1. They have an acid or sour taste.
2. They change blue litmus red.
3. They act upon metals, hydrogen being evolved, its place being taken by the metals, as, for instance:—

$$\underset{\text{Hydrochloric acid.}}{2HCl} + Zn = \underset{\text{Zinc chloride.}}{ZnCl_2} + 2H$$

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + Mn = \underset{\text{Manganese sulphate.}}{MnSO_4} + 2H.$$

4. They act upon metallic hydroxides, forming neutral substances and water as follows:—

$$\underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Potassium hydroxide.}}{KOH} = \underset{\text{Potassium chloride.}}{KCl} + H_2O$$

$$\underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Sodium hydroxide.}}{NaOH} = \underset{\text{Sodium nitrate.}}{NaNO_3} + H_2O$$

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Calcium hydroxide.}}{Ca(OH)_2} = \underset{\text{Calcium sulphate.}}{CaSO_4} + 2H_2O.$$

Hydrogen Acids.—All acids contain hydrogen. They may consist of hydrogen and only one other element, or *of hydrogen and a group of other elements of greater or less complexity. The constitution of those acids which* consist of hydrogen and only one other element is, of course, very simple and readily understood. There are but few examples of this kind, among which are hydrochloric acid, HCl, hydrobromic acid, HBr, sulphydric acid, H_2S, etc. According to our conceptions of the nature of chemical constitution, compounds of the above formulas can have only one constitution.

It is a noticeable fact that acids of this first and simplest class never contain more than two atoms of hydrogen in the molecule, or that no element with a higher hydrogen valency than two forms these simple acids.

Hydroxyl Acids.—By far the greater number of acids belong to the second class mentioned. They consist of hydrogen and a group of greater or less complexity, as, for instance, $H(NO_3)$, nitric acid; $H(ClO_3)$, chloric acid; $H_2(SO_4)$, sulphuric acid, etc. In most acids of this kind, oxygen is one of the constituents of the group, with which the hydrogen is combined.

The hydrogen in these compounds is the changeable constituent. It is readily given up, and metals and groups are taken up in its place. The first question that suggests itself, in considering the constitution of acids, is this: In what manner is the hydrogen in them held in combination? It is believed that investigations, thus far made, justify the answer that the hydrogen in these acids is almost always in combination with oxygen, and, in a very few cases, with that element which is so similar to oxygen, viz., sulphur. The proofs for this statement cannot always be given. In the cases of many acids there exist no independent proofs that, in these, the hydrogen is combined with oxygen. On the other hand, there are so many acids in which it can be satisfactorily shown that the hydrogen is thus combined that the above answer seems to be justified. We accordingly write the formulas of acids in such a way as to indicate the fact of union between oxygen and hydrogen thus:—

$(HO)NO_2$	$(HO)ClO_2$	$(HO)_2SO_2$
Nitric acid.	Chloric acid.	Sulphuric acid.

Or, these same formulas may be made still more definite by writing them as follows:—

$$H—O—NO_2,\quad H—O—ClO_2,\quad \begin{matrix} H—O \\ H—O \end{matrix}\!\!>SO_2.$$

Experimental Evidence.—Under certain circumstances, an atom of oxygen and an atom of hydrogen can be removed from an acid containing oxygen, and one atom of chlorine introduced in the place occupied by the displaced atoms. Now, the simplest conclusion we can draw is that the oxygen and hydrogen were present in the compound as a univalent group, viz., as hydroxyl or —O—H.

Thus,

$$SO_2\!<\!\begin{matrix} OH \\ OH \end{matrix} \text{ yields the compounds}$$

$$SO_2\!<\!\begin{matrix} Cl \\ OH \end{matrix} \qquad \text{and} \qquad SO_2\!<\!\begin{matrix} Cl \\ Cl \end{matrix}$$

Sulphuryl oxichloride. Sulphuryl chloride.

$\text{PO}\begin{array}{l}\diagup\text{OH}\\ -\text{OH}\\ \diagdown\text{OH}\end{array}$	yields	$\text{PO}\begin{array}{l}\diagup\text{Cl}\\ -\text{Cl}\\ \diagdown\text{Cl}\end{array}$.
Phosphoric acid.		Phosphorus oxichloride.
$C_2H_3O(OH)$	yields	C_2H_3O-Cl, etc.
Acetic acid.		Acetyl chloride.

Another reaction, which shows plainly that in these acids hydrogen is intimately associated with oxygen, is that by which the group NH_2 is introduced into them in the place of an atom of oxygen and an atom of hydrogen. The fact *that the elements, oxygen and hydrogen, are displaced together* indicates a connection between them in the compound.

We have the following instances:

$C_2H_3O(OH)$	yields	$C_2H_3O(NH_2)$
Acetic acid.		Acetamide.
$C_7H_5O(OH)$	yields	$C_7H_5O(NH_2)$
Benzoic acid.		Benzamide.

These, with other general reactions, furnish the experimental evidence in favor of the statements above made, *that, in most of those acids which contain oxygen, the* characteristic hydrogen is in combination with oxygen in the form of hydroxyl (OH). In some few cases, as already mentioned, the oxygen is replaced by sulphur.

Further Experiments necessary in most Cases.—If we accept the statement that hydroxyl is present in oxygen acids, we are prepared to take another step. This hydroxyl may be in combination with only one element or with a group of elements. If it is in combination with only one element, the constitution of the resulting acid is easily understood. For instance, in the compound ClOH, hypochlorous acid, only one method of combination suggests itself, viz., Cl—O—H. There are very few examples of this kind.

In those acids in which the hydroxyl is in combination with a group, the constitution is determined when, in addition to showing the presence of hydroxyl, the special constitution of the group itself is determined.

In sulphuric acid, for instance, after having determined

the presence of two hydroxyl groups, we have the formula $SO_2\!<\!\begin{array}{l}OH\\OH\end{array}$; but this formula only partially expresses the constitution of the acid. It remains to be shown in what manner the atoms are combined in the group SO_2, and also, with what atoms the hydroxyl groups are combined. Under the assumption that in sulphuric acid sulphur is sexivalent, and oxygen bivalent, the constitution of the acid is expressed by the formula,

$$\begin{array}{l}O\\O\end{array}\!>\!S\!<\!\begin{array}{l}O-H\\O-H\end{array}.$$

Sulphur Acids.—It has been mentioned that, in some acids, sulphur plays the part which oxygen plays in the hydroxyl acids. In these we have the univalent group (SH). The grounds for assuming the presence of this group in a compound are similar to those which lead to the assumption that the group (OH) is present. The two atoms S and H can both be removed from the compound and be replaced by one univalent atom, as chlorine; and, further, there is a general tendency on the part of these two elements, sulphur and hydrogen, to leave the compound together. Examples of acids of this kind are

$SO_2\!<\!\begin{array}{l}SH\\OH\end{array}$	and	$CN(SH)$.
Thiosulphuric acid.		Sulphocyanic acid.

The compounds formed when the sulphides of tin, arsenic and antimony are dissolved in sulphides of the alkalies are in all probability salts of sulphur acids. There are, for example, the salts,

K_2SnS_3, Na_3AsS_4, Na_3SbS_4.

These are salts of acids of the formulas:—

H_2SnS_3, H_3AsS_4, H_3SbS_4.

These salts and acids are clearly analogous to the better known oxygen compounds:—

K_2SnO_3, Na_3AsO_4, Na_3SbO_4,
H_2SnO_3, H_3AsO_4, H_3SbO_4.

And probably they have a similar constitution, expressed by the formulas:—

$$\begin{array}{l} H{-}S \diagdown \\ \qquad\quad Sn{=}S, \\ H{-}S \diagup \end{array} \qquad \begin{array}{l} H{-}S \diagdown \\ H{-}S{-}As{=}S, \\ H{-}S \diagup \end{array} \qquad \begin{array}{l} H{-}S \diagdown \\ H{-}S{-}Sb{=}S. \\ H{-}S \diagup \end{array}$$

Nitrogen Acids.—Some compounds of carbon that owe their acid properties to the presence in them of hydrogen in combination with nitrogen have long been known. Such, for example, are the so-called acid imides, as succinimide, which, as will be shown further on, has the constitution, $\begin{array}{l} CH_2{-}CO \diagdown \\ | \qquad\qquad\quad NH, \\ CH_2{-}CO \diagup \end{array}$ phthalimide, $C_6H_4\begin{array}{l} \diagup CO \diagdown \\ \qquad\quad NH, \\ \diagdown CO \diagup \end{array}$ benzoic sulphinide, $C_6H_4\begin{array}{l} \diagup CO \diagdown \\ \qquad\quad NH, \\ \diagdown SO_2 \diagup \end{array}$ etc. Then there are some other similar compounds containing the group NH, which also have acid properties, such as, $\begin{array}{l} C_6H_5.CO \diagdown \\ \qquad\qquad NH, \\ C_6H_5.SO_2 \diagup \end{array}$ $\begin{array}{l} CH_3.CO \diagdown \\ \qquad\qquad NH, \\ CH_3.CO \diagup \end{array}$ etc. In general, it may be said that when two of the hydrogen atoms of ammonia are replaced by acid residues, the remaining hydrogen atom has acid properties, or the compound thus formed is an acid.

In the compound azoimide, or hydrazoic acid, HN_3, we have the most remarkable example of the acid character of the group NH. The evidence all goes to show that the structure of this compound is that represented by the formula $\begin{array}{l} N \diagdown \\ \| \quad NH. \\ N \diagup \end{array}$

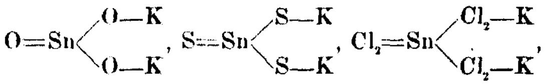
Finally, in one form of cyanic acid it is probable that this imide group is present, as represented thus: $O{=}C{=}N{-}H$; and some facts point clearly to the conclusion that this group is also present in hydrocyanic acid, as shown thus: $C{\equiv}N{-}H$.

Double Halogen Acids.—Many salts are known that are derived from complex acids containing the halogens, fluorine, chlorine, bromine, and iodine. Such, for example, are the salts potassium chloroplatinate, K_2PtCl_6, potassium fluosilicate, K_2SiF_6, sodium chloraurate, $NaAuCl_4$, potas-

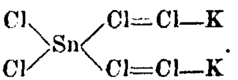
sium chlorstannate, K_2SnCl_6, etc. These salts are commonly called double salts, and no attempt made to explain them. A careful examination has shown that they are analogous to the oxygen and sulphur salts in composition, and in mode of formation, and it seems probable that they are analogous to these better-known salts also in structure. This view necessitates the assumption that a double halogen atom, as Cl_2, Br_2, etc., acts as a bivalent group, playing the same part as oxygen in the double halogen salts. The only objection to this view is that it is based in the polyvalency of the halogen atoms. This objection does not appear to have much weight in view of the fact that the polyvalency of the halogens towards oxygen is now generally accepted. The analogy between the oxygen, the sulphur, and the double halogen compounds is represented in the table given below:—

K_2SnO_3	K_2SnS_3	K_2SnCl_6
K_2PtO_3	—	K_2PtCl_6
$KAlO_2$	—	$KAlCl_4$
K_3AsO_3	K_3AsS_3	K_3AsCl_6
K_2SiO_3	—	K_2SiF_6

As regards the structure of the double halogen atom it seems probable that it is made up thus, —Cl=Cl—, the halogen being trivalent. This is made the more probable by the fact that there are some salts which cannot be explained by the simple assumption represented thus, —Cl—Cl—, whereas they can be explained by the other form. The structural formula of a single double halogen salt will show how the others are to be represented if the hypothesis above, briefly presented, be true. The analogy between the oxygen, sulphur, and double halogen salts is shown by the following formulas:—



or the last may be written thus,



It should be added that several of the double halogens acids are known in the free state as chlorplatinic acid, H_2PtCl_6, chlorauric acid, $HAuCl_4$, etc.

Classification of Acids.—It will be seen that different acids contain different numbers of hydroxyl or other similar groups in their molecules. An acid which contains only one such group in its molecule has, of course, only one acid hydrogen atom. It is called a *monobasic* acid. An acid which contains two such groups in its molecule is a *dibasic* acid. We have, further, *tribasic*, *tetrabasic* acids, etc.

The same distinctions are possible among those acids which consist of hydrogen combined only with an element, and consequently do not contain hydroxyl; but as of these latter acids we have none which contains more than two atoms of hydrogen in the molecule, so we have among them only monobasic and diabasic acids.

Examples:—

Monobasic acids.

HCl, hydrochloric acid.
$NO_2(OH)$, nitric acid.
$Cl(OH)$, hypochlorous acid.

Diabasic acids.

$$SO_2\begin{cases}OH\\OH\end{cases}$$, sulphuric acid.

$$C_2O_2\begin{cases}OH\\OH\end{cases}$$, oxalic acid.

Tribasic acids.

$$PO\begin{cases}OH\\OH\\OH\end{cases}$$, phosphoric acid.

$$AsO\begin{cases}OH\\OH\\OH\end{cases}$$, arsenic acid.

Tetrabasic acids.

$P_2O_3(OH)_4$, pyrophosphoric acid.

Bases.—Bases have properties which may, in general, be said to be the opposite of those of acids. They all contain oxygen and hydrogen, and these elements are combined as hydroxyl, as may be shown in the same way that it was shown for acids. The most striking characteristic of bases is their power to act upon acids, forming neutral substances, and water, as is expressed in the following equations:—

$$\underset{\text{Potassium hydroxide.}}{KOH} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Potassium nitrate.}}{KNO_3} + H_2O;$$

$$\underset{\text{Calcium hydroxide.}}{Ca(OH)_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Calcium sulphate.}}{CaSO_4} + 2H_2O.$$

Almost all bases consist of a metal combined with hydroxyl. A few appear to consist of a group of atoms combined with hydroxyl.

According to the valency of the metals with which the hydroxyl is combined, there are bases with one, two, three, etc., hydroxyl groups in the molecule. Examples of these are the following:—

$K(OH)$, potassium hydroxide.	$Al(OH)_3$, aluminium hydroxide.
$Na(OH)$, sodium hydroxide.	$Cr(OH)_3$, chromium hydroxide.
$Ca(OH)_2$, calcium hydroxide.	$Ti(OH)_4$, titanium hydroxide.
$Ba(OH)_2$, barium hydroxide.	$Zr(OH)_4$, zirconium hydroxide.

Differences between Acids and Bases.—The difference between acids and bases is dependent upon the nature of the elements or groups with which the hydroxyl is combined. The hydroxyl compounds of those elements which have a markedly metallic character are bases. The hydroxyl compounds of those elements which have a markedly non-metallic character are acids. The hydroxyl compounds of those elements which are neither markedly metallic nor non-metallic sometimes act as acids and sometimes as bases. Thus the compound $SbO(OH)$, antimony hydroxide, is a weak base and a weak acid, exhibiting one class of properties or the other, according to the nature of the compound with which it is brought in contact.

Further, a compound consisting of a metal in combination with hydrogen and oxygen, and which has basic properties, may acquire basic properties by an increase in the proportion of oxygen in it. This is illustrated by aluminium hydroxide, $Al(OH)_3$, which is basic, but which acquires acid properties by loss of water. It is thus transformed into the compound $AlO(OH)$, in which the proportion of oxygen relatively to hydrogen is greater than in the basic hydroxide. So, too, while the hydroxide of the formula $Fe(OH)_2$ is basic, the compound $FeO_2(OH)_2$ is acid. A similar fact will be discussed when the carbon compounds are presented. It will then be seen that compounds in which the group $H_2C—O—H$ is present are basic, but that if the proportion of oxygen in the group be increased by the introduction of oxygen in place of the hydrogen the substances thus formed are acid. They contain the group $OC—O—H$.

Complex Bases.—As above stated, there are a few bases which appear to consist of hydroxyl combined with a group of atoms. Such, for instance, are

$BiO(OH)$	$UO_2(OH)_2$	$TiO(OH)_2$
Bismuthyl hydroxide.	Uranyl hydroxide.	Titanyl hydroxide.

These formulas are based upon the assumption that if one molecule of a base has the power to neutralize one molecule of a monobasic acid, it must contain one hydroxyl group; if it can neutralize two molecules of a monobasic or one of a dibasic acid, it must contain two hydroxyls, etc. Now, bismuthyl hydroxide, or the quantity of substance represented by BiO_2H, has the power to neutralize one molecule of a monobasic acid. It is, as we say, a *mon-acid base*, and contains one hydroxyl. Hence the formula $BiO(OH)$ is given to it. We have no means of deciding how the bismuth and oxygen are combined, or whether the hydroxyl is in combination with bismuth or with oxygen. If, however, it be assumed that bismuth is trivalent, and the formula be constructed on the basis of the valency hypothesis we have $O{=}Bi{-}O{-}H$.

Salts.—The neutral substances, to which reference has been made, formed by the action of acids upon bases, are called salts. Salts may be considered either as acids in which the hydrogen has been replaced by a base minus hydroxyl, or as bases in which the hydrogen has been replaced by an acid minus hydroxyl. As the base residues are usually simpler than those of the acids, the former view is most commonly held, although the two views are, of course, identical.

It is a simple matter to deduce the constitution of a salt from that of the acid and base or bases from which it is derived. Usually the hydrogen of the acid is replaced by one or more metals, the latter, as is believed, being held in combination by the same force or forces that held the former. Thus we have

$$SO_2\!<\!\begin{matrix}OH\\OH\end{matrix} \quad \text{and} \quad SO_2\!<\!\begin{matrix}OK\\OK\end{matrix}$$

Sulphuric acid. Potassium sulphate.

$$NO_2{-}OH \quad \text{and} \quad NO_2{-}ONa$$

Nitric acid. Sodium nitrate.

Or, a bivalent element may enter into an acid, in which case two hydrogen atoms will be replaced, thus:—

$$SO_2\begin{matrix}OH\\OH\end{matrix} \quad \text{and} \quad SO_2\begin{matrix}O\\O\end{matrix}Ca;$$

Sulphuric acid. Calcium sulphate.

$$NO_2—OH \quad \text{and} \quad \begin{matrix}NO_2—O\\NO_2—O\end{matrix}>Ba.$$

Nitric acid. Barium nitrate.

Further complications are introduced when trivalent and quadrivalent elements enter into the composition of salts. From what has been said, however, the constitution of these salts will be readily understood.

Complex Salts.—Just as there are some bases, which consist of hydroxyl combined with groups of atoms, so there are salts which may be considered as derived from acids by the replacement of hydrogen by groups of atoms. Thus, a salt obtained from the acid $NO_2—OH$, and the base $UO_2(OH)_2$, probably has the constitution expressed by the formula $\begin{matrix}NO_2—O\\NO_2—O\end{matrix}>UO_2$. Here the hydrogen of the acid is replaced by the group UO_2, which is bivalent.

Anhydrides.—The constituents of water may be abstracted from many acids, and thus a new class of compounds, called anhydrides, is formed. The most striking characteristic of these compounds is their power to form acids with water, or to form salts by direct union with bases. The following are examples of anhydrides: Sulphuric anhydride, SO_3; nitric anhydride, N_2O_5; phosphoric anhydride, P_2O_5; acetic anhydride $(C_2H_3O)_2O$, etc.

When an anhydride is formed from a monobasic acid, two molecules must combine to furnish the hydrogen for the water. After the abstraction of the water, the two acid residues remain united, through the instrumentality of an atom of oxygen, thus:—

$$\left.\begin{matrix}NO_2—OH\\NO_2—OH\end{matrix}\right\} - H_2O = \begin{matrix}NO_2\\NO_2\end{matrix}>O;$$

2 molecules nitric acid. Nitric anhydride.

$$\left.\begin{array}{l} C_2H_3O{-}OH \\ C_2H_3O{-}OH \end{array}\right\} - H_2O = \begin{array}{l} C_2H_3O \\ C_2H_3O \end{array}\!\!>O.$$

2 molecules acetic acid. Acetic anhydride.

When an anhydride is formed from a dibasic acid, a molecule of water may be given off from a molecule of acid, thus:—

$$SO_2\!<\!\begin{array}{l} OH \\ OH \end{array} - H_2O = SO_3;$$

Sulphuric acid. Sulphuric anhydride.

$$CO\!<\!\begin{array}{l} OH \\ OH \end{array} - H_2O = CO_2.$$

Carbonic acid. Carbonic anhydride.

Or, two molecules of a dibasic acid may unite and give off one molecule of water, forming a compound which is, at the same time, an acid and an anhydride, thus:—

$$\left.\begin{array}{l} SO_2\!<\!\begin{array}{l} OH \\ OH \end{array} \\ SO_2\!<\!\begin{array}{l} OH \\ OH \end{array} \end{array}\right\} - H_2O = \begin{array}{l} SO_2\!<\!\begin{array}{l} OH \\ \end{array} \\ \qquad\quad >O \, . \\ SO_2\!<\!\begin{array}{l} \\ OH \end{array} \end{array}$$

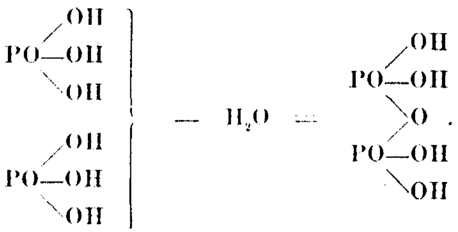
2 molecules sulphuric acid. Pyrosulphuric acid.

When an anhydride is formed from a tribasic acid, several possibilities present themselves. 1. One molecule of the acid may lose one molecule of water, a compound being formed which is anhydride and monobasic acid, thus:—

$$PO\!\begin{array}{l} {-}OH \\ {-}OH \\ {-}OH \end{array} - H_2O = PO_2{-}OH$$

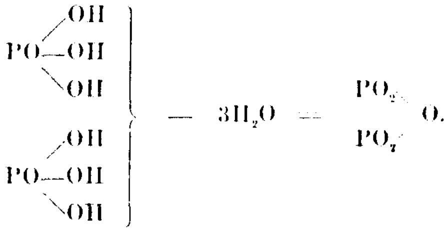
Phosphoric acid. Metaphosphoric acid.

2. Two molecules of the acid may lose one molecule of water, a compound being formed which is a tetrabasic acid, and, at the same time, an anhydride:—



2 mol. Phosphoric acid. Pyrophosphoric acid.

3. Two molecules of the acid may lose three molecules of water, a complete anhydride being formed:—



2 mol. Phosphoric acid. Phosphoric anhydride.

By combining a number of molecules of the acids and abstracting different numbers of molecules of water, a great variety of anhydrides might be produced, at least theoretically. Not many such complicated products are positively known, however.

From tetrabasic acids and acids with even higher basicity, corresponding anhydrides may be derived. With an increase in the basicity of the acids, the complexity of the resulting anhydride is, of course, increased.

Experimental Evidence of the Constitution of Anhydrides.—In regard to the correctness of the formulas given for these anhydrides, it can only be said that they are the simplest conceivable. If it be acknowledged that acetic anhydride $(C_2H_3O)_2O$, consists of two acid residues united by means of an oxygen atom, then, by analogy, it would appear that the other anhydrides, mentioned above, are constituted as represented by the formulas. But can we assume any other formula for acetic anhydride? The acid has the constitution $C_2H_3O(OH)$; the anhydride has the

empirical formula, $C_4H_6O_3$, and is formed by the simple abstraction of water from the acid; it is known that the hydroxyl group has the power to separate from the acid with comparative ease. What, then, is more natural than to assume that the water which is given off from the acid is formed from the hydroxyl groups, and that the groups C_2H_3O remain undecomposed? But this would give us, besides the water, two groups, C_2H_3O and an oxygen atom. These are all combined in one molecule, and, as we believe, in such a way that the oxygen atom joins together the two groups or acid residues, giving the formula

$$\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\Big\rangle O.$$

When an anhydride is formed by the abstraction of water from one molecule of an acid, the simplest conclusion is that an oxygen atom fills the place before occupied by two hydroxyl groups. There is no proof of this, to be sure; but it would be gratuitous to offer any other explanation of the formation of these anhydrides at present.

Oxides.—Just as anhydrides may be obtained from acids by the extraction of water, so the oxides may be regarded as anhydrides of the bases. The consideration of the oxides is simpler than that of the anhydrides, because the bases themselves are generally simpler than the acids.

The simplest oxides are those obtained from the hydroxides of univalent elements, examples of which follow:—

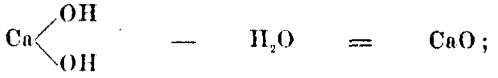
$$\left.\begin{matrix} KOH \\ KOH \end{matrix}\right\} \quad - \quad H_2O \quad = \quad \begin{matrix} K \\ K \end{matrix}\Big\rangle O;$$

2 molecules Potassium hydroxide. — Potassium oxide.

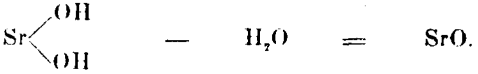
$$\left.\begin{matrix} Na{-}OH \\ Na{-}OH \end{matrix}\right\} \quad - \quad H_2O \quad = \quad \begin{matrix} Na \\ Na \end{matrix}\Big\rangle O;$$

Sodium hydroxide. — Sodium oxide.

Of oxides obtained from the hydroxides of bivalent elements there are, among others, the following:—

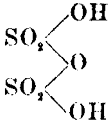


Calcium hydroxide. Calcium oxide.

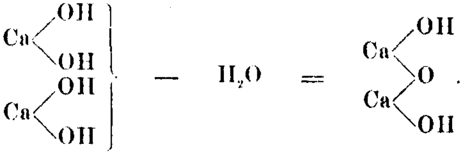


Strontium hydroxide. Strontium oxide.

Theoretically, an intermediate anhydride may be formed, from either of the two preceding oxides, analogous to the formation of pyrosulphuric acid



, from two molecules of sulphuric acid, thus:—



2 mol. Calcium hydroxide. Intermediate anhydride.

Some compounds of this kind are known, derived from copper, iron, etc.

From the hydroxides of trivalent elements more than one oxide may be formed. If one molecule of the hydroxide loses one molecule of water, a substance is formed which is oxide and hydroxide at the same time. Reference has been made to these compounds (see *ante*, p. 128) under the head of bases. The compound AlO—OH may be regarded as derived from the hydroxide $Al(OH)_3$, by the loss of one molecule of water from one molecule of the hydroxide. It is both oxide and hydroxide, and, as has been pointed out, it has acid properties.

The most common method of formation of oxides from hydroxides of trivalent elements consists in the union of two molecules of the hydroxide, which then loses three molecules of water, thus:—

2 mol. Aluminium hydroxide. Aluminium oxide.

The principle of the formation of these oxides is thus seen to be the same as that of the formation of anhydrides. What was said in regard to the constitution of the latter holds good in regard to the constitution of the former. The view stated is the simplest which the facts permit.

Analogy between Salts and Anhydrides and Oxides.—As was seen above, a salt is either an acid in which the hydrogen is replaced by a base residue, or a base in which the hydrogen is replaced by an acid residue. In those salts which are derived from acids containing hydroxyl, a base residue and an acid residue are united by means of oxygen. On the other hand, in many anhydrides two acid residues are united by means of oxygen, while in oxides two base residues are united by means of oxygen.

CHAPTER X.

CONSTITUTION OF CLASSES OF COMPOUNDS OF CARBON.

We have thus briefly considered the different classes of compounds, and have seen upon what foundations our ideas in regard to the general constitution of these classes of compounds rest. Among the compounds of carbon there are many representatives of each of the classes above considered, and all that has been said holds good for these compounds; but, owing to some peculiarities of carbon which distinguish it from the other elements, certain things hold good for the carbon compounds in general, that do not hold good for the corresponding compounds of other elements. In the following paragraphs, therefore, the *general* formulas of the different classes of carbon compounds will be briefly treated.

Hydrocarbons.—Of the compounds of carbon, those which it forms with hydrogen or the hydrocarbons are, in general, the simplest, and of the hydrocarbons, marsh-gas, or methane, CH_4, is the simplest one. With our present ideas in regard to constitution there can be but one formula for this compound, viz:

$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$

which indicates merely that a quadrivalent atom of carbon is saturated by four atoms of hydrogen. This is the most rational supposition that can be made with reference to the compound. The formula is certainly not proved, but it is exceedingly probable. As marsh-gas is a very important member of the group of carbon compounds, and our views regarding the constitution of other hydrocarbons are based very largely upon our conception of marsh-gas, it will be well to inquire more particularly concerning the grounds upon which the above formula is based. The empirical

formula, CH_4, is first established by means of analysis and the determination of the specific gravity of the vapor of the compound. This formula is the expression of a fact and an hypothesis. The fact expressed is that methane contains 75 per cent. carbon and 25 per cent. hydrogen. The hypothesis is that the molecules of all chemical compounds, in the form of gas or vapor, have the same volume as a molecule of hydrogen. This hypothesis tells us the weights of the atoms contained in the molecule of methane and the weight of the molecule of methane, and, hence, further, the number of atoms of carbon and hydrogen contained in the molecule. Knowing the above, it remains for us to determine in what manner these atoms are united, or, what is the same thing, to determine how the atoms are linked together. A study of the various reactions of marsh-gas shows that in all probability each hydrogen exists in the compound independently of the others, that is, not connected with the others. Each one can be removed separately and again introduced. Further, there are no grounds whatever for believing that hydrogen ever acts in any other way than as a univalent element, and the relations of the hydrocarbons can be simply represented only on the assumption that in them the carbon is quadrivalent. Certainly the most plausible hypothesis in regard to the structure of marsh-gas is that expressed by the formula

$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & H \\ & & | & & \\ & & H & & \end{array}$$

which means simply that in the molecule of the compound four atoms of hydrogen are in combination with one carbon atom.

A question which naturally suggests itself in connection with the compound CH_4 is this: Are all the hydrogen atoms combined in the same way in the molecule? In regard to this point, it can only be said that, as far as investigations have gone, an affirmative answer to this question seems justified. If these hydrogen atoms were combined in different ways, then, by replacing different ones by the same element or group, products should be obtained which are not identical. No such results have been reached, although the hydrogen atoms in methane have been replaced in a great variety of ways. It is, indeed, in these facts

that the commonly accepted formula for marsh-gas finds its chief support. The formula

$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

is the only one by which each of the four hydrogen atoms can be represented as bearing the same relation to the carbon atom, if we accept the general method of representation for which the reasons have been given in the introductory remarks on constitution.

Homologous Series.—Starting with methane there is a series of hydrocarbons of the general formula C_nH_{2n+2}. These resemble one another in many respects, and differ from one another in their formulas in a very simple way. The difference between the formulas of any two contiguous members of this series is CH_2. Such a series is called an *homologous series*. A number of similar series are known. In the methane series there are: Methane, CH_4; ethane, C_2H_6; propane, C_3H_8; butane, C_4H_{10}, etc.

The relation between the members of this series is expressed in formulas which represent the carbon atoms combined in what are called open chains. Thus, as has been shown, if two carbon atoms combine in the simplest manner possible, viz., by one of their affinities each, a chain is formed having six free affinities, as follows:

$$\begin{array}{c} |\quad | \\ -C-C- \\ |\quad | \end{array}$$

If three carbon atoms combine in the same way, a chain having eight free affinities is formed, thus:

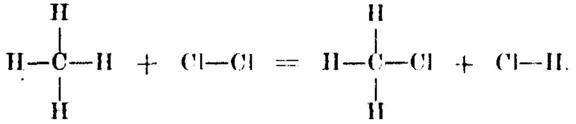
$$\begin{array}{c} |\quad |\quad | \\ -C-C-C- \\ |\quad |\quad | \end{array}$$

In the same way four carbon atoms combining give a chain having ten affinities, etc., etc. By saturating these free affinities with hydrogen we should get compounds of the formulas C_2H_6, C_3H_8, C_4H_{10}, etc., etc., which are the formulas of the hydrocarbons above given.

Experimental Evidence.—Certain experiments have been performed which furnish strong evidence in favor of

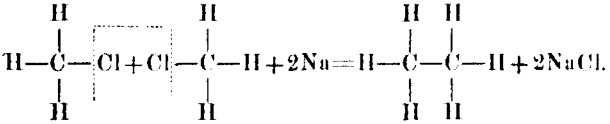
the views in regard to the nature of the combination in the methane series of hydrocarbons.

If methane be treated with chlorine the following reaction takes place :—



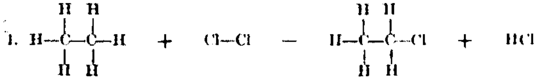
Methane. Chlormethane.

If the product be treated with sodium the chlorine is extracted, and a compound of the formula C_2H_6 is obtained according to the following equation :—

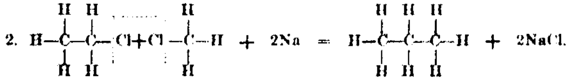


2 molecules Chlormethane. Ethane.

With ethane similar reactions can be realized, and a product, C_3H_8, obtained, thus :—



Ethane. Chlorethane.



Cloréthane. Chlormethane. Propane.

It is plain that, by continuing these reactions with the new compounds obtained, we have it in our power to build up a series of hydrocarbons corresponding to the series given above. If the combination always took place in the manner described, we should have simple chains, in which all the carbon atoms except those at the ends would have two free affinities, while those at the ends would have three free affinities. The hydrocarbons themselves would be represented respectively by the formulas

$H_3C.CH_2.CH_2.CH_3$; $H_3C.CH_2.CH_2.CH_2.CH_3$, etc., etc.

These are called *normal hydrocarbons* to distinguish

them from others of the same general composition, but of different constitution, which will be taken up in a later paragraph.

Alcohols.—Running parallel to the series of hydrocarbons, which have just been considered, is a series of compounds which are regarded as derived from the hydrocarbons by replacing a hydrogen atom in each by the univalent group OH, or hydroxyl. These compounds are to organic chemistry what the hydroxides of the metals are to inorganic chemistry. They are known as *alcohols*. The simplest of these is derived from methane and has

$$\text{the formula } \begin{array}{c} H \\ | \\ H-C-O-H. \\ | \\ H \end{array}$$

Evidence.—One of the hydrogen atoms of those alcohols which contain but one oxygen atom differs from the others. It is easily replaceable by certain groups, known as acid groups, which we shall consider hereafter. It is also replaceable by some metals. In a compound of the formula CH_4O, we must assume that one hydrogen atom is in combination with the oxygen atom, while the other three are not, in order to account for its characteristic behavior. Again, if the alcohol be treated with hydrochloric acid, the oxygen atom and the peculiar hydrogen atom are given off together, and their place is taken by a single atom of chlorine. This shows that the hydrogen and oxygen were present in the form of a univalent group, or as hydroxyl, which is the only form that satisfies these conditions.

$$\underset{\text{Methyl alcohol.}}{H_3C-OH} + \underset{\text{Nitric acid.}}{HO(NO_2)} = \underset{\text{Methyl nitrate.}}{H_3C-O(NO_2)} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Methyl alcohol.}}{H_3C-OH} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Chlormethane.}}{H_3C-Cl} + \underset{\text{Water.}}{H_2O.}$$

$$\underset{\text{Methyl alcohol.}}{H_3C-OH} + \underset{\text{Sodium.}}{Na} = \underset{\text{Sodium methylate.}}{H_3C-ONa} + \underset{\text{Hydrogen.}}{H.}$$

Further, the hydroxyl group can be introduced into the hydrocarbons and the alcohols thus obtained. In order to obtain the alcohol CH_4O, we may start with chlormethane,

CH_3Cl. If this be treated with the hydroxide of silver, the following reaction is realized:—

$$\underset{\text{Chlormethane.}}{CH_3Cl} + Ag(OH) = \underset{\text{Methyl alcohol.}}{CH_3.OH} + AgCl.$$

The above reactions show the correctness of the formula

$$\begin{array}{c} H \\ | \\ H-C-O-H \\ | \\ H \end{array}$$

for the first member of the series of alcohols. Having once recognized the presence of hydroxyl in this alcohol, we should naturally expect to find it in the other alcohols. It is found in them all, and may be detected in the manner indicated in the case just considered.

Classes of Alcohols.—It has been found that there are three classes of alcohols, called, respectively, *primary*, *secondary*, and *tertiary*. These differ very markedly from one another in their properties.

Primary Alcohols.—The differences in the properties of the three classes of alcohols are undoubtedly due to differences in constitution. In all primary alcohols the group CH_2OH, or

$$\begin{array}{c} H \\ | \\ -C-O-H, \\ | \\ H \end{array}$$

is present. This was seen in the case of methyl alcohol, which is a compound of this group with hydrogen, thus:

$$\begin{array}{c} H \\ | \\ H-C-O-H. \\ | \\ H \end{array}$$

In ethyl alcohol, the next member of the series, this group is also present. This follows if the presence of hydroxyl in the alcohols be accepted; for in the compound

$$\begin{array}{ccc} & H & H \\ & | & | \\ H- & C- & C-H, \\ & | & | \\ & H & H \end{array}$$

it makes no difference which hydrogen atom is replaced by

hydroxyl, the resulting compound will, in every case, have the same constitution and will necessarily contain the group $CH_2.OH$. In all primary alcohols the presence of the group $CH_2.OH$ can be proved in a similar way. They are all derived from methyl alcohol by the replacement of a hydrogen atom by hydrocarbon residues of various composition and constitution.

By replacing a hydrogen atom by methyl, CH_3, ethyl alcohol, $CH_3.CH_2.OH$, is obtained.

By replacing a hydrogen atom by ethyl, C_2H_5, propyl alcohol, $C_2H_5.CH_2.OH$, is obtained.

By replacing a hydrogen atom by propyl, C_3H_8, butyl alcohol, $C_3H_8.CH_2.OH$, is obtained, etc.

These alcohols may also be represented by the formulas,

$$C\left\{\begin{array}{l}CH_3\\H\\H\\OH\end{array}\right., \quad C\left\{\begin{array}{l}C_2H_5\\H\\H\\OH\end{array}\right. \text{ and } C\left\{\begin{array}{l}C_3H_8\\H\\H\\OH\end{array}\right.$$

or, in general, any primary alcohol by the formula $C\left\{\begin{array}{l}R\\H\\H\\OH\end{array}\right.$ in which R represents any univalent group, CH_3, C_2H_5, etc., derived from a hydrocarbon.

Secondary Alcohols.—If two hydrogen atoms of methyl alcohol be replaced by hydrocarbon residues, alcohols are obtained which do not contain the group $CH_2.OH$, as is evident from the following examples:—

$$\begin{array}{c}H\\|\\H—C—O—H,\\|\\H\end{array} \qquad \begin{array}{c}CH_3\\|\\H_3C—C—O—H;\\|\\H\end{array} \qquad \begin{array}{c}C_2H_5\\|\\H_3C—C—O—H.\\|\\H\end{array}$$

Methyl alcohol. Isopropyl alcohol. Secondary butyl alcohol.

These substances contain the group CH.OH, and are representatives of secondary alcohols.

The simplest example of this class of substances is isopropyl alcohol, the formula of which is given above.

Secondary alcohols may also be represented by such formulas as the following:—

$C\begin{cases}CH_3\\CH_3\\H\\OH\end{cases}$, $C\begin{cases}CH_3\\C_2H_5\\H\\OH\end{cases}$, $C\begin{cases}C_2H_5\\C_2H_5\\H\\OH\end{cases}$, etc., or, in general, by the formula $C\begin{cases}R\\R'\\H\\OH\end{cases}$, in which R and R′ may be the same or different univalent hydrocarbon groups.

Evidence in favor of the General Formula of Secondary Alcohols.—There are two alcohols of the formula, C_3H_8O. One of these conducts itself like the primary alcohols, and hence in all probability contains the group $CH_2.OH$. An alcohol isomeric with the primary alcohol cannot contain the group $CH_2.OH$, but must contain the group $CH.OH$, as may be readily shown. Both of the alcohols are derived from the same hydrocarbon, $\begin{array}{c}\quad H\quad H\quad H\\ \quad |\quad\;\; |\quad\;\; |\\ H—C—C—C—H\\ \quad |\quad\;\; |\quad\;\; |\\ \quad H\quad H\quad H\end{array}$. In this hydrocarbon there appear to be only two kinds of hydrogen atoms, viz., those in combination with the central carbon atom, and those in combination with the terminal carbon atoms. If any one of the latter be replaced by hydroxyl, primary propyl alcohol containing the group $CH_2.OH$ is formed. Whereas, if one of the former hydrogen atoms be replaced by hydroxyl, secondary propyl alcohol containing the group $CH.OH$. is obtained. Only these two cases are possible.

But, again, this secondary alcohol is prepared by allowing nascent hydrogen to act upon acetone. It will be shown that acetone must be represented by the formula $\begin{array}{l}CH\\ |\\ CO\\ |\\ CH_3\end{array}$. Now, in its conversion into secondary propyl alcohol, acetone takes up two atoms of hydrogen, and the only place where these hydrogen atoms can find entrance into the above molecule, if the carbon is quadrivalent, is in combination with the central carbon atom. If the oxy-

gen atom is linked to the carbon atom, as in carbon monoxide, a condition which is represented by the formula C=O, we can conceive of the relation between the carbon and oxygen being changed by the action of hydrogen, so that a group HC—O—H may be formed. This is what is believed to take place. This addition of hydrogen changes the relation between the carbon and the oxygen and saturates them:—

$$\begin{array}{c} C \\ \| \\ O \end{array} + \begin{array}{c} H \\ \\ H \end{array} = \begin{array}{c} CH \\ | \\ OH \end{array}.$$

Similar considerations, in connection with other secondary alcohols, lead to similar results, and hence the conclusion is drawn that all secondary alcohols contain the group CH.OH, or that they are derived from methyl alcohol by the replacement of two hydrogen atoms by univalent hydrocarbon groups

Tertiary Alcohols.—If three hydrogen atoms of methyl alcohol be replaced by hydrocarbon residues, alcohols are obtained which contain neither the group CH_2OH, nor the group CH.OH, as is shown by the following formulas:—

$$\begin{array}{c} H \\ | \\ H—C—O—H, \\ | \\ H \end{array} \quad \begin{array}{c} CH_3 \\ | \\ CH_3—C—O—H, \\ | \\ CH_3 \end{array} \quad \begin{array}{c} C_2H_5 \\ | \\ CH_3—C—O—H. \\ | \\ CH_3 \end{array}$$

Methyl alcohol. Tertiary butyl alcohol. Tertiary amyl alcohol.

These substances contain the group C.OH, and are representatives of tertiary alcohols.

The simplest example of this class of alcohols is tertiary butyl alcohol, $C_4H_{10}O$, the constitution of which is indicated by the formula given above.

The tertiary alcohols may also be represented by such formulas as $C\left\{\begin{array}{l} CH_3 \\ CH_3 \\ CH_3, \\ OH \end{array}\right.$ $C\left\{\begin{array}{l} CH_3 \\ C_2H_5 \\ C_2H_5, \\ OH \end{array}\right.$ $C\left\{\begin{array}{l} C_2H_5 \\ C_2H_5 \\ C_3H_8, \\ OH \end{array}\right.$ etc., or, in general, by the formula $C\left\{\begin{array}{l} R \\ R' \\ R'', \\ OH \end{array}\right.$ in which R, R′ and

R″ may be the same or different univalent hydrocarbon residues.

Experimental Evidence.—The evidence for the formula

$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—OH \\ | \\ CH_3 \end{array}$$

for the simplest tertiary alcohol is this:—

There is a hydrocarbon, the formula of which can be shown to be

$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_3. \\ | \\ H \end{array}$$

From this two alcohols are derived, one of which conducts itself as a primary alcohol, while the other does not. The former must have the formula

$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_2—OH. \\ | \\ H \end{array}$$

The only alcohol derived from the hydrocarbon which is not a primary alcohol must have the formula

$$\begin{array}{c} CH_3 \\ | \\ CH_3—C—CH_3, \\ | \\ O \\ | \\ H \end{array}$$

and hence contains the group

$$\begin{array}{c} | \\ —C—OH, \\ | \end{array}$$

which is trivalent. Further, similar considerations of other tertiary alcohols indicate that in them also the group C.OH is contained, and, consequently, this is looked upon as the characteristic group of these compounds.

Very strong confirmatory evidence in favor of the commonly accepted views as to the structure of the three classes of alcohols is furnished by the study of the changes which they undergo when treated with oxidizing agents, as will be shown farther on.

Mercaptans.—If, in place of hydroxyl, in the alcohols the group HS be introduced, substances called mercaptans are obtained. These are, in many respects, analogous to alcohols, though in their reactions they differ from them somewhat. Their constitution is similar to that of the alcohols. The principal method for their formation consists in the action of potassium sulphydrate, KSH, on the chlorides of hydrocarbon residues, the reaction taking place as follows:—

$$\underset{\text{Chloride.}}{RCl} + K{-}SH = \underset{\text{Mercaptan.}}{R{-}SH} + KCl.$$

Theoretically, a mercaptan may be prepared corresponding to every alcohol. Thus we might have primary, secondary, and tertiary mercaptans, corresponding to all the known primary, secondary, and tertiary alcohols. Only such mercaptans as correspond to the primary alcohols have been prepared up to the present.

Acids.—What has already been said concerning acids in general is true of the acids of carbon. They contain hydroxyl, and possess the general properties of acids. In general, they are weaker than other acids, though they differ in strength between comparatively wide limits. There are several series of acids of carbon, corresponding to the series of hydrocarbons and alcohols. The simplest carbon acid is derived from methane, and has the formula

$$\begin{array}{c} H \\ | \\ O{-}C{-}O{-}H \end{array}$$

. It differs from the simplest alcohol in containing an atom of oxygen in the place of two atoms of hydrogen. This is clearly shown by writing the formulas of the alcohol and of the acid side by side in this way:—

$$\underset{\text{Alcohol.}}{\begin{array}{c} H \\ | \\ H_2{=}C{-}O{-}H \end{array}} \qquad \underset{\text{Acid.}}{\begin{array}{c} H \\ | \\ O{=}C{-}O{-}H. \end{array}}$$

Just as the alcohol consists of hydrogen combined with the group $CH_2.OH$, so the acid consists of hydrogen combined with the group $CO.OH$. This is the characteristic group of the acids of carbon

Experimental Evidence.—In the first place, the presence of hydroxyl is proved as in the case of ordinary acids. Assuming the presence of hydroxyl for reasons already given, the formula of the acid, H_2CO_2, becomes HCO—OH. Further, the other hydrogen atom contained in the acid does *not conduct itself as if it were in combination with oxygen*, but rather like hydrogen atoms, which are in combination with carbon directly. No changes which the acid undergoes indicate any connection between this hydrogen and oxygen, and we may therefore conclude that they are not present as hydroxyl. But, if they are not present as hydroxyl, they must be united directly with the carbon atom, and the formula is

$$\begin{array}{c} H \\ | \\ O{-}C{-}O{-}H \end{array}$$

Now, by certain reactions, it is possible to replace that hydrogen atom in the acid which is in direct combination with the carbon by groups such as CH_3, C_2H_5, etc. The compounds thus obtained must contain the group CO.OH. They possess all the properties of acids.

Methods for the Formation of the Acids of Carbon.—The methods of preparation of the acids of carbon throw light upon their constitution. Some of these methods are here briefly described.

1. The simplest acid, above referred to, viz., formic acid, H_2CO_2, is obtained by bringing carbon monoxide, CO, together with potassium hydroxide, KOH. The two substances combine directly, yielding the potassium salt of the above acid, thus:—

$$CO + KOH = HCO_2K.$$

From this experiment we conclude that, in the salt, one of the oxygen atoms is in direct combination with carbon, as it was in carbon monoxide, while the other oxygen atom serves the purpose of linking the carbon atom to potassium. Hence the group

$$COOK \text{ or } \begin{array}{c} O{-}C{-}O{-}K \\ | \end{array}$$

is present in the salt, and the group

$$\begin{array}{c} O{-}C{-}O{-}H \\ | \end{array} \text{ in the acid.}$$

This proof is unsatisfactory, for a similar argument might

be used to show that the hydrogen in the salt, HCO_2K, is in direct combination with oxygen.

2. When certain hydrocarbons are allowed to act upon carbonyl chloride, $COCl_2$, one of the chlorine atoms is replaced by a residue, as may be illustrated thus:—

$$(I.)\quad CH_4 + COCl_2 = CH_3.COCl + HCl.$$

When the product is treated with water, the second chlorine atom is replaced by OH, as follows:—

$$(II.)\quad CH_3.COCl + HHO = CH_3.CO\,OH + HCl.$$

Now carbonyl chloride is obtained by the direct addition of chlorine, Cl_2, to carbon monoxide, CO; and hence has the constitution $CO\begin{smallmatrix} \diagup Cl \\ \diagdown Cl \end{smallmatrix}$. The simplest interpretation of reaction (I.) above is that the residue CH_3 takes the place occupied by one of the chlorine atoms, which would give $CO\begin{smallmatrix} \diagup CH_3 \\ \diagdown Cl \end{smallmatrix}$. Lastly, the simplest interpretation of reaction (II.) is that the hydroxyl group enters in the place of the second chlorine atom, which gives us the constitution of the product $CO\begin{smallmatrix} \diagup CH_3 \\ \diagdown OH \end{smallmatrix}$. This product is acetic acid, a homologue of the simplest acid of carbon. It contains the group CO.OH.

3. The compound cyanogen, $\begin{array}{c} CN \\ | \\ CN \end{array}$, is converted into an acid by the action of water. This acid has the formula $C_2H_2O_4$. It is a dibasic acid and hence contains two hydroxyl groups, which would lead to the formula $C_2O_2(OH)_2$. As both the hydroxyl groups conduct themselves in exactly the same way, it is concluded that they are combined in exactly the same way. The only formula that satisfies these conditions is $\begin{array}{c} OH \\ | \\ CO \\ | \\ CO \\ | \\ OH \end{array}$. In this compound there are two

groups CO.OH, and, as we have seen, it is a dibasic acid. There are a great many compounds, containing the group CN acting as a univalent group. By treating these with solutions of metallic hydroxides, the nitrogen is given off in the form of ammonia, NH_3, and in its place two atoms of oxygen and one atom of a univalent element are taken up. The group, with which the CN is in combination, remains unchanged. Hence, in accordance with the above experiment, it is believed that this reaction consists in a conversion of the group CN into COOH or COOM, in which M represents one atom of a univalent metal. The constitution of this group is, of course, expressed as above by the formula $\underset{|}{O{-}C{-}OH}$. All the substances thus prepared, and containing this group, are derivatives of the acids; they are salts.

The methods of formation and the reactions of the organic acids lead then to the conclusion that they are made up as indicated in the general formula $CO\left\langle\begin{matrix}R\\OH\end{matrix}\right.$ or $C\left\{\begin{matrix}R\\O\\OH\end{matrix}\right.$, according to which they are derivatives of carbonic acid, $CO\left\langle\begin{matrix}OH\\OH\end{matrix}\right.$, being derived from it by the introduction of a residue R in place of one hydroxyl of the acid. The relations between a primary alcohol, a cyanide, and an acid, are shown by the following formulas:—

$$C\left\{\begin{matrix}R\\H,\\H\\OH\end{matrix}\right. \qquad C\left\{\begin{matrix}R\\ \\N\end{matrix}\right. \qquad C\left\{\begin{matrix}R\\O\\OH\end{matrix}\right. .$$

Aldehydes.—Aldehydes are products formed by the partial oxidation of primary alcohols, the group CH_2OH being converted into COH. This group is not identical with the group $-\overset{|}{\underset{|}{C}}-O-H$ of tertiary alcohols, but has the constitution expressed by the formula $O{-}\overset{|}{C}{-}H$. It is univalent, just as the group CH_2OH, from which it is

derived, is univalent; whereas, the tertiary alcohol group, COH, is trivalent. The aldehydes are intermediate products between primary alcohols and the acids which these yield. It was shown that the acids are formed from these alcohols by the extraction of hydrogen and addition of oxygen. If hydrogen is abstracted, and no oxygen added, the product is an aldehyde, thus:—

$R—CH_2OH$,	$R—COH$,	$R—COOH$.
Primary alcohol.	Aldehyde.	Acid.

Experimental Evidence.—The proofs of the general constitution of aldehydes are similar to those given for the acids. Take, for instance, the simplest aldehyde. This has the formula H_2CO. The reactions of the substance show that hydroxyl is not present. If treated with the chlorides of phosphorus the oxygen of an aldehyde is replaced by two chlorine atoms. This shows that the oxygen is held in combination by the carbon atom in quite a different way from that which is characteristic of hydroxyl, and, consequently, it cannot be in combination with hydrogen, forming hydroxyl. This leads to the formula $\begin{array}{c} \quad H \\ \quad | \\ O—C—H \end{array}$ or $\begin{array}{c} \quad H \\ \quad | \\ O{=}C—H \end{array}$ for the above compound. It consists of a hydrogen atom combined with the group $\begin{array}{c} H \\ | \\ —C—O \end{array}$. Other aldehydes are derived from this simplest one by replacing one of the hydrogen atoms by a residue of greater or less complexity. Thus, the group CH_3 or C_2H_5 may be introduced, and the compounds $CH_3—COH$, and $C_2H_5—COH$, formed, both of which are aldehydes.

The methods for the preparation of aldehydes also furnish evidence in favor of the constitution above ascribed to them. Some of these are the following:—

1. It has already been seen that, when an acid is treated with the chloride of phosphorus, its hydroxyl is replaced by an atom of chlorine. Each such chloride, as was shown, contains the group $\begin{array}{c} Cl \\ | \\ —C—O \end{array}$. If the chlorine atom in this group could be replaced by hydrogen, the characteristic

aldehyde group $\begin{array}{c} H \\ | \\ -C-O \end{array}$ would plainly be formed. Such a replacement has been effected in the case of some of the chlorides, and the resulting compounds have been found to be the expected aldehydes.

2. When a salt of any acid of carbon is mixed with a salt of the simplest acid of carbon (formic acid), of the formula H.CO.OH, and the mixture distilled, an aldehyde is formed, together with a carbonate. The carbonates are derived from a dibasic acid, and have the formula $CO\!\left\langle\begin{array}{l} OM \\ OM \end{array}\right.$. It seems rational to suppose that the groups OM have passed directly from the compounds in which they were originally contained to the carbonate, and that the group CO has also been derived directly from one of the original acids. If these suppositions be correct, then we are led to the conclusion that the aldehyde resulting from the described reaction contains the group $\begin{array}{c} H \\ | \\ C-O \end{array}$. For, let R—CO.OM represent the formula of any salt of a carbon acid, and H.CO.OM a salt of formic acid. On bringing these two compounds together and heating them, either one of two things can take place if the above suppositions be correct. The groups forming the carbonate may be split off thus:—

$$\begin{array}{l} R-CO-OM \\ H-CO-OM \end{array} ;$$

or, thus:

$$\begin{array}{l} R-CO-OM \\ H-CO-OM \end{array} .$$

The remaining groups, uniting in the simplest way, will give, in either case, a compound, $\begin{array}{c} H \\ | \\ R-C-O \end{array}$.

The relation between a primary alcohol, and the corre-

sponding aldehyde and acid, is shown by the following formulas:—

$$C \left\{ \begin{array}{l} R \\ H \\ H \\ OH \end{array} \right. \qquad C \left\{ \begin{array}{l} R \\ H \\ O \end{array} \right. \qquad C \left\{ \begin{array}{l} R \\ OH \\ O \end{array} \right.$$

Alcohol. Aldehyde. Acid.

Acetones.—Acetones are products of the partial oxidation *of secondary alcohols, the group* $\begin{array}{c} | \\ -C-OH \\ | \\ H \end{array}$ *being converted into* $\begin{array}{c} | \\ CO \\ | \end{array}$. The aldehydes, too, contain the group $\begin{array}{c} | \\ CO \\ | \end{array}$; but it is further characteristic of aldehydes that one of the affinities of this group is saturated with hydrogen, giving the complete group $\begin{array}{c} | \\ CO \\ | \\ H \end{array}$. On the other hand, it is characteristic of acetones that both of the affinities of the group $\begin{array}{c} | \\ CO \\ | \end{array}$ are saturated with hydrocarbon residues. Thus the simplest acetone has the formula $\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{array}$, both of the affinities of the characteristic group being saturated with residues of the hydrocarbon methane, CH_4.

Experimental Evidence.—As just stated, the simplest acetone has the formula C_3H_6O. If a chloride of phosphorus be allowed to act upon this compound, the result is similar to that obtained in the same experiment with aldehydes, viz., the atom of oxygen is abstracted, and two chlorine atoms take its place. This shows that the oxygen was not present as hydroxyl, but was combined with the

carbon atom, as in carbon monoxide, forming the group $\overset{|}{\underset{|}{\text{CO}}}$.

Again, if nascent hydrogen be allowed to act upon this acetone, secondary propyl alcohol is the product, and the alcohol has the formula

$$\begin{array}{l} \text{CH}_3 \\ | \\ \text{C} \left\langle \begin{array}{l} \text{OH} \\ \text{H} \end{array} \right. \\ | \\ \text{CH}_3 \end{array}$$

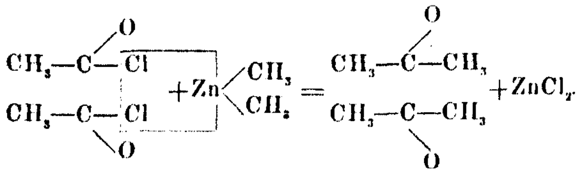
From this we may conclude that in acetone, as well as in secondary propyl alcohol, the two groups CH_3 are present; and we are thus led to the formula

$$\begin{array}{l} \text{CH}_3 \\ | \\ \text{CO} \\ | \\ \text{CH}_3 \end{array}$$

for the simplest acetone. It plainly consists of two hydrocarbon residues combined by means of the bivalent group $\overset{|}{\underset{|}{\text{CO}}}$.

The following methods of preparation serve as evidence of the accepted constitution of acetones:—

1. Just as aldehydes are obtained from acid chlorides by replacing the chlorine by hydrogen, so acetones are obtained from the same chlorides by replacing the chlorine by hydrocarbon residues. By treating acetyl chloride, $C_2H_3O.Cl$, with zinc methyl, $Zn(CH_3)_2$, ordinary acetone, $CO(CH_3)_2$, is produced together with zinc chloride, $ZnCl_2$. The formula of acetyl chloride is known to be $CH_3—\overset{\displaystyle O}{\overset{/}{C}}—Cl$. The simplest interpretation of the above reaction is that a methyl group of zinc methyl takes the place of a chlorine atom in acetyl chloride, thus:—



And this leads clearly to the formula above given for acetone.

2. When the salts of many acids of carbon are subjected to dry distillation, acetones are formed, together with a carbonate or carbonates. This reaction is analogous to the reaction for the preparation of aldehydes, by the distillation of a mixture of the salt of some carbon acid and a salt of formic acid. What has been said in regard to the latter reaction, showing that the group $\overset{|}{\underset{|}{C}}—O$ must be present in aldehydes, holds good in regard to the reaction under consideration, and shows just as conclusively that the group $\overset{|}{\underset{|}{C}}—O$ must be present in acetones. Let R.CO.OM represent a salt of an acid of carbon. Its decomposition by heat may be represented as follows:

$$\begin{array}{l} R.|CO.OM| \\ R.CO.|OM| \end{array}$$

The residues uniting, a compound, R—CO—R, is formed, which has the general formula of an acetone. Or let R.COOM represent the salt of one carbon acid and R'.COOM the salt of another carbon acid, in which R and R' are both hydrocarbon residues. The decomposition, which takes place when a mixture of these two salts is heated, is represented as follows:

$$\begin{array}{l} R.|COOM| \\ R'.CO|OM| \end{array}$$

This gives a compound of the formula R—CO—R'.

It will be seen that one of the first conditions for the production of an acetone by means of this reaction is that neither of the salts employed be a formate, H.COOM, as the use of the latter would lead to the formation of an aldehyde.

The facts that when a primary alcohol is oxidized it is first converted into an aldehyde and then into an acid; that a secondary alcohol first yields acetone and then breaks down; and that a tertiary alcohol yields neither acetone nor aldehyde, but breaks down—these facts are in perfect accordance with the views held regarding the

constitution of the compounds, and find a ready interpretation by their aid. To make this clear a few words of explanation are necessary. It has been found that, when a hydrocarbon of the general formula $C\begin{cases}R\\R'\\R''\\H\end{cases}$ is treated with an oxidizing agent, the three residues at first resist the action and the hydrogen atom is changed to hydroxyl. From a study of a large number of facts it appears clear that, whenever a compound containing hydrogen in combination with carbon is oxidized, the first change brought about is the change of hydrogen to hydroxyl. Assuming this to be the case, the first change of a primary alcohol would be represented thus:

$$C\begin{cases}R\\H\\H\\OH\end{cases} + O = C\begin{cases}R\\H\\OH\\OH\end{cases}.$$

But the compound thus formed evidently represents an unstable condition. Compounds containing two hydroxyls in combination with one carbon give up water readily, as is seen in the case of ordinary carbonic acid, $CO\begin{matrix}/OH\\ \backslash OH\end{matrix}$, which, as is well known, loses water spontaneously, and is thus converted into carbon dioxide CO_2. If this change should take place in the compound represented above, the result would be an aldehyde $C\begin{cases}R\\H\\O\end{cases}$. Now, by further oxidation, the remaining hydrogen would be changed to hydroxyl, and the product would be an acid, $C\begin{cases}R\\OH\\O\end{cases}$.

As regards the oxidation of secondary alcohols to acetones a similar explanation holds good. The secondary alcohol, $C\begin{cases}R\\R'\\H\\OH\end{cases}$, would first be converted into the com-

pound $C\begin{cases} R \\ R' \\ OH \\ OH \end{cases}$; but this would at once lose the elements of water, and thus be converted into an acetone $C\begin{cases} R \\ R' \\ O \end{cases}$. This could not undergo the second change necessary to the formation of an acid, but if any further change should take place it would involve the breaking down of the residues.

Finally, it is clear that neither the formation of an aldehyde, of an acid, nor of an acetone is possible in the case of a tertiary alcohol if the formulas above given are correct.

The first change which we should expect to take place on the oxidation of a tertiary alcohol, $C\begin{cases} R \\ R' \\ R'' \\ OH \end{cases}$, would be the breaking down of one of the residues.

Similar changes take place in a number of other cases. Thus, the phosphines and mercaptans undergo change in the same general way, but in these cases the phenomena are complicated by the fact that the valency of phosphorus and of sulphur is greater towards oxygen than towards hydrogen. The analogy between the three cases will be clear from the following considerations:—

Marsh-gas, $C\begin{cases} H \\ H \\ H \\ H \end{cases}$, is changed to carbonic acid, $C\begin{cases} OH \\ OH \\ O \end{cases}$;

A derivative of marsh-gas, $C\begin{cases} R \\ H \\ H \\ H \end{cases}$, is changed to an acid, $C\begin{cases} R \\ OH \\ O \end{cases}$;

Phosphine, $P\begin{cases} H \\ H \\ H \end{cases}$, is changed to phosphoric acid, $P\begin{cases} OH \\ OH \\ OH \\ O \end{cases}$;

A derivative of phosphine, $P\begin{cases} R \\ H \\ H \end{cases}$, is changed to a phosphinic acid, $P\begin{cases} R \\ OH \\ OH \\ O \end{cases}$;

Sulphuretted hydrogen, $S \begin{cases} H \\ H \end{cases}$, is changed to sulphuric acid, $S \begin{cases} OH \\ OH \\ O \\ O \end{cases}$;

A mercaptan, $S \begin{cases} R \\ H \end{cases}$, is changed to a sulphonic acid, $S \begin{cases} R \\ OH \\ O \\ O \end{cases}$.

Ethereal Salts.—In general when acids and bases act upon each other salts are formed, water being eliminated. So, also, when alcohols and carbon acids act upon each other, compounds similar to salts are formed, water being eliminated:

$$\underset{\text{Formic acid.}}{H.COOH} + \underset{\text{Alcohol.}}{C_2H_5.OH} = \underset{\text{New compound.}}{H.CO.OC_2H_5} + H_2O;$$

$$\underset{\text{Sulphuric acid.}}{SO_2\begin{matrix} \diagup OH \\ \diagdown OH \end{matrix}} + \underset{\text{Methyl alcohol.}}{2CH_3.OH} = \underset{\text{New compound.}}{SO_2\begin{matrix} \diagup O.CH_3 \\ \diagdown O.CH_3 \end{matrix}} + 2H_2O.$$

$$\underset{\text{Nitric acid.}}{NO_2—OH} + \underset{\text{Alcohol.}}{C_2H_5—OH} = \underset{\text{New compound.}}{NO_2—OC_2H_5} + H_2O.$$

It will be seen that these compounds differ from salts in that they contain hydrocarbon residues in the place of metals. Salts were defined as acids in which the hydrogen of the hydroxyl group is replaced by a base residue. These compounds are acids in which the hydrogen of the hydroxyl group is replaced by a hydrocarbon residue. All compounds of this kind are called ethereal salts. The analogy between ethereal salts and ordinary salts is very close, and, if the nature of the latter is understood, that of the former will also be clear. There are ethereal salts derived from monobasic, dibasic, tribasic acids, etc., and there are ethereal salts containing univalent, bivalent, trivalent, etc., hydrocarbon residues; for example,

Ethereal salts of monobasic acids:—

$$\underset{\text{Ethyl nitrate.}}{NO_2.O.C_2H_5}, \qquad \underset{\text{Methyl acetate.}}{CH_3.CO.OCH_3}, \text{ etc.}$$

Ethereal salts of dibasic acids:—

$$\underset{\text{Methyl sulphate.}}{SO_2 \begin{cases} OCH_3 \\ OCH_3 \end{cases}}, \qquad \underset{\text{Ethyl succinate.}}{C_2H_4 \begin{cases} CO.O\,C_2H_5 \\ CO.O.C_2H_5 \end{cases}}, \text{ etc.}$$

Ethereal salts of tribasic acids:—

$$PO\left\{\begin{array}{l}O.C_2H_5\\O.C_2H_5,\\O.C_2H_5\end{array}\right. \qquad C_3H_5\left\{\begin{array}{l}CO.O.C_2H_5\\CO.O.C_2H_5,\\CO.O.C_2H_5\end{array}\right. \text{etc.}$$

Ethyl phosphate. Ethyl tricarballylate.

The above-mentioned ethereal salts all contain univalent hydrocarbon residues. Among those containing bivalent residues may be mentioned:—

$$\left.\begin{array}{l}CH_3.CO.O\\CH_3.CO.O\end{array}\right\} C_2H_4.$$

Ethylene diacetate.

The ordinary fats are examples of ethereal salts containing a trivalent residue:—

$$\left.\begin{array}{l}C_{15}H_{31}.CO.O\\C_{15}H_{31}.CO.O\\C_{15}H_{31}.CO.O\end{array}\right\} C_3H_5 \quad \text{and} \quad \left.\begin{array}{l}C_{17}H_{35}.CO.O\\C_{17}H_{35}.CO.O\\C_{17}H_{35}.CO.O\end{array}\right\} C_3H_5.$$

Glyceryl tripalmitate, or Palmitin. Glyceryl tristearate, or Stearin.

Experimental Evidence.—The fact that ethereal salts are, in many cases, formed by the direct action of acids upon alcohols, and that water is formed at the same time, taken together with the knowledge we possess regarding the constitution of acids and alcohols, points clearly to the constitution given above for these ethers. But another method of formation furnishes more decisive evidence.

If the silver salts of acids are treated with the chlorides, bromides, or iodides of hydrocarbon residues, ethereal salts are formed in which the residues plainly occupy the place which was occupied by the silver in the salts, and the silver itself is found in combination with the chlorine, bromine, or iodine which was in combination with the hydrocarbon residues. This is seen in the following typical reactions:—

$$\underset{\text{Silver acetate.}}{CH_3.CO.OAg} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl acetate.}}{CH_3.CO\,O.C_2H_5} + AgI.$$

$$\underset{\text{Silver succinate.}}{C_2H_4\begin{array}{l}\diagup CO.Ag\\\diagdown CO.Ag\end{array}} + \underset{\text{Methyl iodide.}}{2CH_3I} = \underset{\text{Methyl succinate.}}{C_2H_4\begin{array}{l}\diagup CO.OCH_3\\\diagdown CO.OCH_3\end{array}} + 2AgI.$$

Ethers.—The ethers are the analogues of the metallic oxides. They consist of two hydrocarbon residues, united

by means of an oxygen atom, just as the metallic oxides consist of two basic residues united by means of an oxygen atom. Examples of these are the following:—

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!O, \qquad \begin{matrix} C_2H_5 \\ CH_3 \end{matrix}\!\!>\!O, \qquad \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!O, \text{ etc.}$$

Methyl ether. Methyl-ethyl ether. Ethyl ether.

Experimental Evidence.—The constitution of these compounds is rendered clear by a consideration of one of the principal methods for their formation.

When an alcohol is treated with sodium or potassium, as we have seen, the hydrogen of the hydroxyl is replaced by the metal. Compounds, such as sodium ethylate, $C_2H_5.ONa$, sodium methylate, $CH_3.ONa$, etc., are thus obtained. If these compounds are further treated with the iodides of hydrocarbon residues, the iodine combines with the metal and the residues unite:—

$$\underset{\text{Sodium ethylate.}}{C_2H_5.ONa} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Ethyl ether.}}{C_2H_5{-}O{-}C_2H_5} + NaI,$$

$$\underset{\text{Sodium methylate.}}{CH_3.ONa} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Methyl ether.}}{CH_3{-}O{-}CH_3} + NaI,$$

$$\underset{\text{Sodium methylate.}}{CH_3.ONa} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = \underset{\text{Methyl-ethyl ether.}}{CH_3{-}O{-}C_2H_5} + NaI,$$

$$\underset{\text{Sodium ethylate.}}{C_2H_5.ONa} + \underset{\text{Methyl iodide.}}{CH_3I} = \underset{\text{Methyl-ethyl ether.}}{C_2H_5{-}O{-}CH_3} + NaI.$$

From these reactions it is seen what the constitution of the ethers formed must be. It appears that in each case the hydrocarbon residue enters into the new compound in the place occupied by the metal, and, according to our conceptions concerning alcohols, this metal is united to the rest of the molecule in which it is contained by means of an oxygen atom.

Anhydrides.—The anhydrides of carbon compounds are derived from carbon acids in the same way that anhydrides in general are derived from acids; and all the possibilities which were considered above hold good for these anhydrides. There are anhydrides derived from monobasic, dibasic, tribasic acids, etc. There are partial and

complete anhydrides; but, further, there are anhydrides derived from compounds which partake of the double character of alcohol and acid. In these compounds the hydroxyl which imparts the alcoholic character, and that which imparts the acid character, both together furnish the elements which form the water given off.

CHAPTER XI.

CONSTITUTION OF SUBSTITUTION PRODUCTS.

We have thus far had to deal with the various classes of chemical compounds which are known to exist, and it has been shown that each class is characterized by some peculiarity of constitution which is recognized in each member of the class. There is in each compound a peculiar grouping of atoms that determines its character, making it an acid or an alcohol, an acetone or an aldehyde, etc. As long as this group remains unchanged, the compound belongs to the same class. If the group is changed, the compound loses its characteristics and belongs to another class. On the other hand, the hydrocarbon residues, with which the class groups are united, may undergo a variety of changes without interfering with the general properties of the compounds. The most common of these changes are those which are effected by substitution.

Chemical compounds act upon one another, in general, in two ways: 1st. They unite directly, forming only one product, as in the following reactions:—

$$\underset{\text{Ammonia.}}{NH_3} + HCl = \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

$$\underset{\text{Ethylene.}}{C_2H_4} + Br_2 = \underset{\text{Ethylene bromide.}}{C_2H_4Br_2}$$

2d. They exchange certain constituents, forming two or more new products, thus:—

$$\underset{\text{Ethane.}}{C_2H_6} + Cl_2 = \underset{\text{Chlorethane.}}{C_2H_5Cl} + HCl$$

$$\underset{\text{Aldehyde.}}{CH_3.COH} + 6Cl = \underset{\text{Trichloraldehyde.}}{CCl_3.COH} + 3HCl$$

$$\underset{\text{Benzene.}}{C_6H_6} + H_2SO_4 = \underset{\text{Benzenesulphonic acid.}}{C_6H_5.SO_3H} + H_2O$$

$$\underset{\text{Benzene.}}{C_6H_6} + HNO_3 = \underset{\text{Nitrobenzene.}}{C_6H_5(NO_2)} + H_2O.$$

The latter kind of action is by far the most common. *It* is called substitution. In the above examples, the principal products are called substitution products, though, strictly speaking, both products are substitution products.

While the act of substitution is involved in nearly all chemical reactions, and hence nearly all chemical compounds may be considered as substitution products with reference to some other compounds, still it is customary to include under this head only those which are formed by the replacement of hydrogen in carbon compounds, and the substitutions which are spoken of, are those which can be actually effected—not imaginary cases.

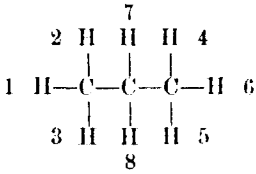
Substitution Products containing Chlorine, Bromine, or Iodine.—The simplest examples of substitution products are those which are formed by the action of the so-called halogens (Cl, Br, I) on carbon compounds. The action consists in the abstraction of one or more atoms of hydrogen from the compound, and, as is believed, the filling of the places thus left vacant by a corresponding number of atoms of the substituting element. The action is that of displacement. The constitution of the products is the same as that of the compounds from which they are derived. Thus when chlorine acts upon acetic acid, $CH_3.CO.OH$, the following reactions take place successively:—

$$\begin{aligned} CH_3.CO.OH &+ Cl_2 = CH_2Cl.CO.OH + HCl. \\ CH_2Cl.CO.OH &+ Cl_2 = CHCl_2.CO.OH + HCl. \\ CHCl_2.CO.OH &+ Cl_2 = CCl_3.CO.OH + HCl. \end{aligned}$$

The constitution of the three products is the same as that of the acid from which they are derived.

Among the simple substitution products, however, differences are possible, and are actually observed, which are not possible in the original compounds. Take, for example, the compound propane, C_3H_8. The constitution of this hydrocarbon is $\begin{array}{c} \quad H \;\; H \;\; H \\ \quad | \quad\; | \quad\; | \\ H-C-C-C-H \\ \quad | \quad\; | \quad\; | \\ \quad H \;\; H \;\; H \end{array}$. According to our fundamental conceptions in regard to constitution, the hydrogen atoms cannot be arranged in any other way

with reference to the carbon atoms. There is only one hydrocarbon of this composition possible. But the carbon atoms in the compound differ from one another. The two, which are represented in the formula as ending the chain, are alike, while the central atom differs from them. The first are in combination with carbon by means of only one affinity each, while the central atom is joined to carbon by means of two affinities. We should naturally expect, then, that the difference between these two kinds of carbon atoms would cause a difference between the hydrogen atoms combined with them. If such a difference exists, then different products must be obtained according as a hydrogen atom attached to one of the terminal carbon atoms is replaced, or another hydrogen atom attached to the central carbon atom. Thus, if in a compound of the following formula,



any one of the hydrogen atoms, numbered 1, 2, 3, 4, 5, 6, be replaced by some other element, such as chlorine, the resulting compound should in each case be the same.

If, however, one of the hydrogen atoms numbered 7 or 8 be replaced by the same element as in the first case, a compound of the same composition, but of different constitution, should be obtained. The formulas of the two compounds would be respectively

$$CH_2Cl.CH_2.CH_3 \quad \text{and} \quad CH_3.CHCl.CH_3.$$

Thus, it is seen that the position of a substituting element must be taken into consideration in studying the constitution of compounds. In connection with the individual compounds, which will be briefly considered in a subsequent chapter, the methods will be described which make the determination of the position of substituting atoms and groups possible.

Complex Substitution Products.—Under this head are included all those products which are formed by replacing

the hydrogen of a carbon compound either partially or wholly by groups of atoms. In accordance with what has just been said concerning the simple substitution products, it is plain that, in studying the constitution of the complex substitution products, two things must be taken into consideration:—

1st. The constitution of the substituting group itself, and,

2d. The position of the group in the molecule of the substitution product.

Only the first part of the problem will be taken up here.

Constitution of Substituting Groups.—The groups which we shall have to consider are the following: The cyanogen group CN, and an isomeric group; the sulphonic acid group SO_3H; the nitro group NO_2; the nitroso group NO; the amido group NH_2; the imido group NH; and a few other groups intimately connected with those mentioned.

Constitution of the Group CN.—That acid of carbon, which consists of a nitrogen atom and a hydrogen atom, united with a carbon atom, viz., hydrocyanic acid, has already been referred to. By appropriate reactions it is possible to transfer the group CN, contained in hydrocyanic acid, to other compounds in such a way that it takes the place of hydrogen, forming a substitution product. It is expressed by the formula —C—N. We have the following reactions:—

$$\underset{\text{Monochloracetic acid.}}{CH_2Cl.COOH} + \underset{\text{Potassium cyanide.}}{KCN} = \underset{\text{Cyanacetic acid.}}{CH_2(CN).COOH} + KCl;$$

$$\underset{\text{Ethylene bromide.}}{C_2H_4Br_2} + \underset{\text{Potassium cyanide.}}{2KCN} = \underset{\text{Ethylene cyanide.}}{C_2H_4(CN)_2} + 2KCl.$$

Those substitution products which consist only of the group —C—N combined with a hydrocarbon residue, are called *cyanides* or *nitriles*.

Other compounds are known, which have the same composition as the nitriles, but a different constitution. They are known as *isonitriles*, *isocyanides*, or *carbamines*. The difference between the cyanides and carbamines is believed to consist in the fact that in the former the carbon of the group CN is the linking atom, while in the latter the nitro-

gen performs this function. This difference is expressed, in the case of the ethyl compounds, by the formulas $C_2H_5—C—N$ for the cyanide, and $C_2H_5—N—C$ for the isocyanide. These formulas are based upon the reactions of the two classes of compounds. The reactions are as follows:—

Ethyl cyanide, $C_2H_5.CN$, when treated with an alkali, yields propionic acid $C_2H_5.CO.OH$. The nitrogen is given off, and oxygen and hydrogen take its place. The carbon remains united to the residue C_2H_5. The conclusion is therefore drawn that in the cyanide the carbon atom of the group CN is directly united with the hydrocarbon residue. For, if it had not been, the removal of the nitrogen ought to have caused the formation of a product containing a smaller number of carbon atoms than the cyanide itself. The reaction which does take place is the one considered above, which gives rise to the formation of acids from the cyanides, viz:—

$$\underset{\text{Ethyl cyanide.}}{C_2H_5CN} + 2H_2O = \underset{\text{Propionic acid.}}{C_2H_5.COOH} + NH_3.$$

If the group CN were in combination with the hydrocarbon residue by means of the nitrogen atom, we should expect the nitrogen atom to remain in combination with the hydrocarbon residue, in case of decomposition, or we should expect the nitrogen atom to take with it the carbon atom, with which it is most intimately combined. In either case, a separation of the carbon atoms would be the result, and we should obtain products containing a smaller number of carbon atoms than the original compound contained. This is exactly what takes place when the carbamines are decomposed. When treated with hydrochloric acid, they yield two products; one of these is formic acid, a compound containing one atom of carbon; the other consists of the hydrocarbon residue of the original compound combined with the nitrogen atom and hydrogen. Thus in the case of ethyl isocyanide, the decomposition is represented as follows:—

$$\underset{\text{Ethylcarbamine.}}{C_2H_5—N—C} + 2H_2O = \underset{\text{Ethylamine.}}{\left.\begin{matrix}C_2H_5\\H\\H\end{matrix}\right\}N} + \underset{\text{Formic acid.}}{H.COOH}$$

The fact that the compound $N\begin{cases} C_2H_5 \\ H \\ H \end{cases}$, in which the nitrogen atom is evidently in combination with the hydrocarbon residue, is so readily formed, leads to the conclusion that the same kind of union exists in the isocyanide. The fact, further, that one carbon atom is given off so readily from the molecule, indicates clearly that it was held in combination in some manner different from that in which the other carbon atoms of the molecule are held in combination.

In the terms of the valency hypothesis, the difference between the cyanides and carbamines is expressed by the general formulas $R—C \equiv N$ for the cyanides, and $R—N \equiv C$ for the isocyanides. In the one case the nitrogen is believed to act as a triad, in the other as a pentad.

Constitution of the Group SO_3H.—By the action of concentrated sulphuric acid upon hydrocarbons and various other compounds containing hydrogen, derivatives are obtained, which differ from the original compounds in containing the group SO_3H in the place of hydrogen. The reaction consists in the formation of water and the new derivative, thus:—

$$C_6H_6 + SO_2\begin{cases} OH \\ OH \end{cases} = SO_2\begin{cases} C_6H_5 \\ OH \end{cases} + H_2O.$$

Benzene. Benzenesulphonic acid.

These products all act like acids in every way, so that we are justified in assuming the presence of hydroxyl in them. As they are formed so readily from sulphuric acid, it is also fair to assume that the group SO_2OH is a residue of sulphuric acid. Then, if the constitution of sulphuric acid is known, the constitution of this group may be inferred. The fact that it is a residue of sulphuric acid is shown also in the following way: By replacing one of the hydroxyl groups of sulphuric acid by an atom of chlorine, a compound of the formula $SO_2\begin{cases} Cl \\ OH \end{cases}$ is obtained, which, by simple treatment with water, is reconverted into sulphuric acid. There can be little doubt that the group SO_2OH of this chloride has exactly the same constitution as the

corresponding group of the acid. But, if this chloride be allowed to act upon benzene, benzenesulphonic acid and hydrochloric acid are the products, the former having all the properties possessed by the benzenesulphonic acid formed by the action of sulphuric acid on benzene. The reaction takes place thus:—

$$C_6H_6 + SO_2\begin{cases}Cl \\ OH\end{cases} = C_6H_5.SO_2.OH + HCl.$$

Here, evidently, the group $SO_2.OH$ of the chloride takes the place of an atom of hydrogen in benzene.

Assuming then the general formula $SO_2.OH$ for the group, it remains to decide in what manner the atoms of the sub-group SO_2 are united. The first question to be answered, and perhaps the only one that can be answered by experimental methods at present, is, whether in the compound containing the group SO_2, as, for example, $C_6H_5.SO_2.OH$, the sulphur is in direct combination with the hydrocarbon or not.

When the sulphonic acids are reduced, they yield, as final products, the corresponding sulphydrates. Thus, $C_6H_5.SO_3H$ yields C_6H_5SH. Further, when the sulphydrates are oxidized, they yield sulphonic acids: $C_2H_5.SH$ yields $C_2H_5.SO_3H$, etc. The simplest interpretation of these facts is found in the assumption that the sulphur is in direct combination with the hydrocarbon, as represented in the formulas:—

$$C_2H_5—S—H,\ C_2H_5—S—O_2—OH,\ C_6H_5—S—H \text{ and } C_6H_5—S—O—OH.$$

It is impossible to determine with any degree of certainty whether the two oxygen atoms (O_2) are both in direct combination with sulphur or not, though the opinion is now commonly held that in the sulphonic acids the sulphur acts as a hexad and that the constitution is expressed by the general formula $R—\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{S}}—O—H$. This question is intimately connected with that in regard to the constitu-

tion of sulphuric acid, and this will be discussed further on.

Constitution of the Group NO_2.—When concentrated nitric acid acts upon hydrocarbons, etc., hydrogen is frequently replaced by the group NO_2, thus:—

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{NO_2OH} = \underset{\text{Nitrobenzene.}}{C_6H_5.NO_2} + H_2O$$

The reaction, as will be noticed, is similar to that which takes place when sulphuric instead of nitric acid is used. Just as in the former case it may be assumed that the group SO_3H is a residue of sulphuric acid, so in the latter case it may be assumed that the group NO_2 is a residue of nitric acid. The formula that we accept for nitric acid will show us the constitution of the group NO_2. Again, nitro compounds are formed by treating a chloride, bromide, or iodide of a hydrocarbon residue with silver nitrite, $AgNO_2$, the reaction taking place as follows:—

$$\underset{\text{Ethyl iodide.}}{C_2H_5I} + AgNO_2 = \underset{\text{Nitroethane.}}{C_2H_5(NO_2)} + AgI.$$

It would appear from the latter reaction that the group NO_2 has the same constitution in the nitro derivatives that it has in nitrous acid; but this is not the case, or, at least, certain facts seem to indicate clearly a difference between the groups.

There are two series of compounds of the same composition, but of different constitution, both of which contain the group NO_2. The members of one of these series are ethereal salts of nitrous acid. If nitrous acid contains hydroxyl, then the ethereal salts have the general constitution R—O—NO, in which R represents a hydrocarbon residue. The characteristic feature in the constitution of these ethereal salts is the same as that which we find in all ethereal salts, viz., the acid group is combined with the hydrocarbon residue by means of an *atom of oxygen*. That this is true of the ethereal salts of nitrous acid is shown by the fact that, when nascent hydrogen acts upon them, they yield the alcohols corresponding to the hydrocarbon residues which they contain, and at the same time ammonia. If the nitrogen atom were directly united with the hydrocarbon residue, we should probably find it in combination with this residue after the above reduction.

The decomposition which actually takes place is represented thus:—

Ether, R—O—NO, yields—

$$\underset{\text{Alcohol.}}{R\text{—}O\text{—}H} \quad \text{and} \quad \underset{\text{Ammonia.}}{H\text{—}N\begin{matrix} \diagup H \\ \diagdown H \end{matrix}}.$$

With the constitution assumed for the ethereal salt, it is evident that the formation of an alcohol by the addition of hydrogen would necessitate the splitting off of the group containing nitrogen.

On the other hand, the second series of compounds are not ethereal salts, but true substitution products. They consist of hydrocarbon residues combined with the group NO_2 by means of the *nitrogen atom*. Their general constitution is expressed by the formula $R\text{—}NO_2$.

This conclusion is reached by a study of the products of the reduction of nitro compounds. When treated with nascent hydrogen, they yield products known as amine bases, which have been shown to be ammonia in which one hydrogen atom has been replaced by a hydrocarbon residue. The decomposition is represented as follows:—

$$\underset{\text{Nitro product.}}{R\text{—}NO_2} + 6H = \underset{\text{Amine base.}}{R\text{—}NH_2} + 2H_2O.$$

In the product obtained in this case, it is evident that the nitrogen atom is in direct combination with the hydrocarbon residue, and hence we may assume that this kind of combination also existed in the original nitro compound.

Accepting the above formula for nitro compounds, it is difficult to see how they can be formed by the reaction with silver nitrite. For, if the hydrocarbon residue took the place occupied by the silver in the salt, it is plain that the product would be an ethereal salt, which, according to what has already been said, must have the formula R—O—NO. The product, however, is not an ethereal salt. Consequently, some other change besides that of an interchange of places by the silver atom and the hydrocarbon residue must be accomplished at the same time. Consequently, further, the group NO_2 in nitrous acid has

a constitution differing from that of the group NO_2 of nitro compounds.*

As regards the constitution of these two groups, in nitrous acid there is, in the first place, in all probability one hydroxyl. This gives one oxygen atom combined with hydrogen on the one hand, and, on the other, with nitrogen, thus: H—O—N—. The only thing additional that is present in the molecule is an atom of oxygen, which it is safe to suppose is combined with nitrogen; whence we have the group—O—N—O or (—O—N=O) as the characteristic group of the acid and its derivatives. But the group of nitro compounds unites with residues by means of its nitrogen atom, as has been seen. Hence we can conceive of two formulas for the group NO_2, viz., $-\mathrm{N}\!<\!\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}$, in which the nitrogen is trivalent, and $-\mathrm{N}\begin{matrix}\mathrm{=O}\\ \mathrm{=O}\end{matrix}$, in which the nitrogen is quinquivalent. It has not been found possible to decide which of these two formulas is the correct one. The latter, $-\mathrm{N}\begin{matrix}\mathrm{=O}\\ \mathrm{=O}\end{matrix}$, is now more commonly accepted than the former. The essential difference between these formulas is that in one the two oxygen atoms are represented as united with each other, and in the other they are represented as only in combination with nitrogen. Our experimental methods of investigation are not subtle enough to cope with this question.

Constitution of the Group NO.—There are two classes

* It has been suggested that when an iodide, as, for example, ethyl iodide, C_2H_5I, acts upon silver nitrite, $AgNO_2$, the reaction takes place in two stages. First, an addition-product is formed as represented in the equation:

$$\mathrm{Ag{-}O{-}N{=}O} + \mathrm{C_2H_5I} = \begin{array}{l}\mathrm{Ag{-}O{-}N{-}O}\\ \qquad\quad | \;\; |\\ \qquad\;\; \mathrm{C_2H_5I}\end{array}.$$

Second, this addition-product breaks down into a nitro compound and silver iodide:

$$\begin{array}{l}\mathrm{Ag{-}O{-}N{-}O}\\ \qquad\quad | \;\; |\\ \qquad\;\; \mathrm{C_2H_5I}\end{array} = \begin{array}{l}\mathrm{O{=}N{=}O}\\ \quad\;\; |\\ \quad \mathrm{C_2H_5}\end{array} + \mathrm{AgI}.$$

of compounds, both of which contain a group NO. They are the *nitroso* and the *isonitroso* compounds. The former can be prepared by treating with nitrous acid compounds which contain the so-called imido group NH, or those which contain the group CH. If, on the other hand, compounds which contain the group CH_2 are treated with nitrous acid, isonitroso compounds are formed. The fact that the nitroso compounds are converted into nitro compounds by oxidation, and into amido compounds containing NH_2, points to an analogy with these substances. They are hence represented by the general formula R—NO.

The isonitroso compounds are made by treating with hydroxylamine, NH_3O, compounds which contain the acetone or aldehyde group, CO. The reaction may be represented in two ways, according as we assume the presence of hydroxyl in hydroxylamine, or not:—

$$X^* - CO + HHHNO = X-C\begin{matrix} H \\ NO \end{matrix} + H_2O$$

$$X - CO + H_2NOH = X-C-N-OH + H_2O.$$

The results of experiments on the subject indicate that in the isonitroso compounds the relations between the elements are expressed by the formula X—C—N—OH, or X=C=N—OH. A simple example of the isonitroso compounds is furnished by acetoxime, which is formed by the action of hydroxylamine on acetone, as represented in the equation:—

$$\begin{matrix} CH_3 \\ | \\ CO \\ | \\ CH_3 \end{matrix} + H_2NOH = \begin{matrix} CH_3 \\ | \\ C=N-O-H \\ | \\ CH_3 \end{matrix} + H_2O.$$

The aldoximes which are formed by the action of hy-

* X simply represents whatever the carbonyl CO group is in combination with.

droxylamine on aldehydes are also isonitroso compounds. A simple example is that formed from ordinary aldehyde:—

$$\begin{array}{c} CH_3 \\ | \\ CO \\ | \\ H \end{array} + H_2NOH = \begin{array}{c} CH_3 \\ | \\ C{=}N{-}O{-}H \\ | \\ H \end{array} + H_2O.$$

Constitution of the Group NH_2.—Compounds containing the group NH_2 are called *amido compounds*, or primary amines. The group is plainly a residue of ammonia and is univalent, having the constitution $-N\begin{matrix} H \\ H \end{matrix}$. These compounds are readily obtained by the action of nascent hydrogen on nitro derivatives, the group NO_2 being converted into NH_2. Amido substitution products have properties similar to those of ammonia, which fact furnishes further evidence of a similarity in the constitution of the two. They have basic properties in the same sense that ammonia has basic properties, *i. e.*, they unite directly with all acids, forming salts. In addition to the above method of formation, there is also the action of aqueous ammonia upon chlorides, bromides, or iodides of hydrocarbon residues:—

$$\underset{\text{Ethyl bromide.}}{C_2H_5Br} + NH_3 = \underset{\text{Ethylamine.}}{C_2H_5(NH_2)} + HBr.$$

This latter method indicates very clearly the intimate connection between amido compounds and ammonia.

Constitution of the Group NH.—Finally, there is a class of compounds called *imido compounds*, or secondary amines. These contain the group NH, which is bivalent, and hence occupies the place of two hydrogen atoms. Like amido compounds, they may be considered as derived from ammonia by the replacement of two hydrogen atoms by hydrocarbon residues. The constitution of the group and of the compounds is readily understood. We have:—

$$\underset{\text{2 mol. Ethyl bromide.}}{\left.\begin{array}{c} C_2H_5Br \\ C_2H_5Br \end{array}\right\}} + NH_3 = \underset{\text{Diethylamine.}}{\left.\begin{array}{c} C_2H_5 \\ C_2H_5 \\ H \end{array}\right\} N} + 2HBr.$$

Just as there are primary, secondary, and tertiary alcohols derived from methyl alcohol by the replacement of one, two, or three hydrogen atoms by hydrocarbon residues, so there are primary, secondary, and tertiary amines derived from ammonia by the replacement of one, two, or three atoms of hydrogen by hydrocarbon residues. The general formulas of the three classes of amines are:—

$$N\begin{cases}R\\H\\H\end{cases},\qquad N\begin{cases}R\\R'\\H\end{cases},\quad\text{and}\quad N\begin{cases}R\\R'\\R''\end{cases}.$$

Primary amine.	Secondary amine.	Tertiary amine.

Constitution of the Groups N_2H_3 and N_2H_2.—The hydrazine compounds are closely allied to the amines. They bear the same relation to hydrazine,* N_2H_4, that the amines bear to ammonia. Diethylhydrazine $(C_2H_5)_2N_2H_2$, is prepared by starting from diethylamine $(C_2H_5)_2NH$. When this is treated with nitrous acid a nitroso compound $(C_2H_5)_2N(NO)$, is formed. By reduction the nitroso compound is converted into the corresponding amido compound $(C_2H_5)_2N—NH_2$, which is diethylhydrazine.

The various classes of chemical compounds which have thus been studied are the principal classes with which we have to deal. There are a few other classes, among which are the so-called *mustard oils*, the *diazo compounds*, and the *quinones*. These will be taken up later, in connection with better known compounds with which they are most closely allied.

In classifying compounds we have distinguished between general classes and their substitution products. This distinction is generally justified, though, in a certain sense, even those compounds which belong to the general classes are substitution products, or, at least, may be considered as such. This is particularly the case with the compounds of carbon, all of which may be considered as derived from certain hydrocarbons by the introduction of various groups.

* This compound, or rather a hydrate of it of the composition, $N_2H_4.H_2O$, has recently been prepared. This hydrate is a gas which acts in many respects like ammonia.

Thus the alcohols are derived from hydrocarbons by replacing hydrogen by hydroxyl, OH; the acids by replacing hydrogen by carboxyl, CO.OH, etc. Speaking, then, of all the groups which have been studied as substituting groups, the general statement may be made that: In all substituting groups the characterizing element or elements may be replaced by another or others of the same general character. Thus, as we have already seen, oxygen may be replaced by sulphur. Further, sulphur may, in some cases, be replaced by selenium or tellurium; nitrogen may be replaced by phosphorus, etc. Thus new compounds are formed, but the constitution of these is the same as that of the compounds from which they are derived, and hence they require no separate treatment in this place.

CHAPTER XII.

SPECIAL STUDY OF THE CONSTITUTION OF CHEMICAL COMPOUNDS.

FROM what has been said in the preceding chapters the constitution of the majority of compounds will be understood. In this chapter the constitution of individual compounds will be treated so far as they require separate treatment. In this section the compounds of carbon will demand our principal attention, because more is known concerning their constitution than is known concerning other compounds, and indeed all our ideas regarding the constitution of the so-called inorganic compounds are for the most part applications of ideas gained in the study of the compounds of carbon.

COMPOUNDS NOT CONTAINING CARBON, OR INORGANIC COMPOUNDS.

The compounds which the univalent elements, hydrogen, chlorine, bromine, iodine, fluorine, sodium, potassium, lithium, cæsium, rubidium, silver, form with one another appear to have the simplest constitution of which we have any conception. They require no study here.

Compounds of Chlorine, etc., with Oxygen, and with Oxygen and Hydrogen.—Hydrogen peroxide has the empirical formula H_2O_2. If in this compound the oxygen is bivalent, the simplest arrangement of the atoms is that represented in the formula H—O—O—H. There is indeed no independent evidence of the correctness of this formula, but no other formula expresses the constitution at all satisfactorily, and hence this is accepted as correct.

The acids which chlorine forms with oxygen and hydro-

gen have already been treated incidentally in connection with the subject of valency. It was then shown that the most probable view is that in all these acids except hypochlorous acid, $HOCl$, the chlorine is polyvalent. Thus, chlorous acid is believed to be correctly represented by the formula $O=Cl-O-H$ in which the chlorine is trivalent, chloric acid by

$$\begin{array}{c} O \\ \| \\ Cl-O-H \\ \| \\ O \end{array}$$

in which the chlorine is quinquivalent, and perchloric acid by the formula

$$\begin{array}{l} \;\;\;O \\ \;\;\;\| \\ O=Cl-O-H \\ \;\;\;\| \\ \;\;\;O \end{array}$$

in which the chlorine is septivalent. As has been pointed out, these acids are regarded as derived from hydroxyl compounds by the elimination of water. A large number of salts of periodic acids are known which cannot readily be explained on any other assumption but that they are derived from a number of acids which in turn are derivatives of the acid $I(OH)_7$, mainly of the acid $OI(OH)_5$ or $O=I(OH)_5$ in which the iodine appears to be septivalent.

Compounds of Sulphur, etc., with Oxygen, and with Oxygen and Hydrogen.—Sulphur forms a number of compounds with oxygen and hydrogen, some of which have been carefully studied. The compounds with oxygen alone are sulphur dioxide, SO_2, and sulphur trioxide, SO_3. Without indulging in any unnecessary speculation, the simplest view in regard to these compounds is that in them sulphur is respectively quadrivalent and sexivalent. This view is represented in the following formulas: $O=S=O$ and

$$\begin{array}{c} O \\ \| \\ O=S=O \end{array}$$

For this there is just as good reason as for the view that in carbon dioxide the carbon is quadrivalent as represented by the formula $O=C=O$. If it could be shown that in these oxides of sulphur the oxygen atoms are in combination with one another, the above formulas would of course have to be abandoned. But this has not

been shown, nor is there the slightest reason for making the assumption. The periodicity of valency which has been discussed makes the view that sulphur is sexivalent towards oxygen appear highly probable.

The acids of sulphur are the following:—

H_2SO_3, *sulphurous acid.*
H_2SO_4, sulphuric acid.
$H_2S_2O_7$, pyrosulphuric acid.
$H_2S_2O_3$, thiosulphuric acid.
$H_2S_2O_6$, *dithionic acid.*
$H_2S_3O_6$, trithionic acid.
$H_2S_4O_6$, tetrathionic acid.
$H_2S_5O_6$, pentathionic acid.

Sulphurous Acid, H_2SO_3.—This acid is not known except in water solution, though a large number of its metallic and ethereal salts have been made. From a study of these derivatives conclusions have been drawn concerning the constitution of the acid itself. It is possible to conceive of two arrangements of the atoms composing sulphurous acid, both representing dibasic acids. One of these arrangements is this, $O{=}\overset{\overset{\Large H}{|}}{\underset{\underset{\Large O}{\|}}{S}}{-}O{-}H$, in which the sulphur is represented as sexivalent; the other is this, $H{-}O{-}\overset{\overset{\Large O}{\|}}{S}{-}O{-}H$, in which the sulphur is represented as quadrivalent. The evidence points clearly to the first formula. First, the acid forms two different salts of the formula $NaKSO_3$. This would not be possible if it had the constitution represented by the second formula, in which plainly each of the two hydrogen atoms bears the same relation to the molecule. Again, the sulphonic acids are easily made by treating salts of sulphurous acid with halogen substitution-products of the hydrocarbons, as, for example:—

$$C_2H_5I + NaSO_3H = C_2H_5.SO_3H + NaI.$$

Further, it has already been shown (see Sulphonic

Acids, *ante*), that in the sulphonic acids the sulphur is in all probability in direct combination with the hydrocarbon residues. This makes it, in turn, appear probable that in the sulphite used in the above reaction the metal is in direct combination with sulphur. Finally, starting with a salt of a sulphonic acid, as $C_2H_5.SO_2.ONa$, the metal can be replaced by ethyl, and thus a compound obtained which probably has the constitution

$$\begin{array}{c} C_2H_5 \\ | \\ O{=}S{-}O{-}C_2H_5 \\ \| \\ O \end{array};$$

and, on the other hand, starting with the oxy-chloride $O{=}S\begin{cases} Cl \\ Cl \end{cases}$, and treating this with ethyl alcohol, a product is obtained which probably has the constitution $O{=}S\begin{cases} O{-}C_2H_5 \\ O{-}C_2H_5 \end{cases}$.

This is isomeric with the product obtained from the sulphonic acid. The evidence is therefore in favor of the view that sulphurous acid has the constitution—

$$\begin{array}{c} H \\ | \\ O{=}S{-}O{-}H \\ \| \\ O \end{array} \quad \text{or} \quad S\begin{cases} H \\ OH \\ O \\ O \end{cases}.$$

Sulphuric Acid, H_2SO_4.—Reactions which have been discussed make the presence of two hydroxyl groups in sulphuric acid appear probable. We thus have the formula $SO_2\begin{cases} OH \\ OH \end{cases}$. We cannot, however, by experiment determine the constitution of the group SO_2. It is now commonly believed to have the constitution expressed by the formula $O{=}S{=}O$, and sulphuric acid itself is regarded as

$$\begin{array}{c} O{-}H \\ | \\ O{=}S{=}O \\ | \\ O{-}H \end{array},$$

in which the sulphur is sexivalent.

This formula can be tested with reference to one point, and that is as to whether both hydroxyl groups bear the same relation to the molecule. If they do, it should not be possible to prepare two isomeric ethereal salts containing two different hydrocarbon residues. If two ethereal salts of the composition $SO_2\begin{cases} CH_3 \\ C_2H_5 \end{cases}$, for example, could be prepared, this would furnish evidence in favor of the view that sulphuric acid is unsymmetrical, or that the two hydroxyls bear different relations to the molecule. This view would be expressed in a formula of this kind, $S\begin{cases} OH \\ O{-}O{-}OH \end{cases}$ or $O{=}S\begin{cases} OH \\ O{-}OH \end{cases}$. When sulphuric acid is treated with phosphorus pentachloride under proper conditions one hydroxyl is replaced by chlorine and a compound of the formula $SO_2\begin{cases} Cl \\ OH \end{cases}$ is formed. When this is treated with alcohols ethereal salts are formed. With methyl alcohol and ethyl alcohol, for example, the reactions represented in the following equations take place:—

$$SO_2\begin{cases} Cl \\ OH \end{cases} + CH_3OH = SO_2\begin{cases} OCH_3 \\ OH \end{cases} + HCl;$$

and $$SO_2\begin{cases} Cl \\ OH \end{cases} + C_2H_5OH = SO_2\begin{cases} OC_2H_5 \\ OH \end{cases} + HCl.$$

When the compounds thus formed are treated with phosphorus pentachloride the hydroxyl is replaced by chlorine, and the products are represented by the formulas $SO_2\begin{cases} OCH_3 \\ Cl \end{cases}$ and $SO_2\begin{cases} OC_2H_5 \\ Cl \end{cases}$. Finally, when these are treated with alcohols, neutral ethereal salts of sulphuric acid are formed. If the former be treated with ethyl alcohol and the latter with methyl alcohol the reactions represented in the following equations take place:—

$$SO_2\begin{cases} OCH_3 \\ Cl \end{cases} + C_2H_5OH = SO_2\begin{cases} OCH_3 \\ OC_2H_5 \end{cases} + HCl;$$

and $$SO_2\begin{cases}OC_2H_5\\Cl\end{cases} + CH_3OH = SO_2\begin{cases}OC_2H_5\\OCH_3\end{cases} + HCl.$$

It may fairly be assumed that the methyl and ethyl groups in one of these compounds occupy the same places relatively to the molecule that the ethyl and methyl groups do in the other; or the group OCH_3 in the first compound and the group OC_2H_5 in the second occupy the place of the same hydroxyl of sulphuric acid; and the same is probably true of the group OC_2H_5 in the first compound and the group OCH_3 in the second. If, then, there is any difference between the two hydroxyls of sulphuric acid, the two compounds should be isomeric; whereas, if there is no difference, the two hydroxyls bear the same relation to the molecule, and the two compounds should be identical.

Experiment has shown that there is no difference between the ethereal salts prepared as above described, and hence the conclusion is drawn that the constitution of sulphuric acid should be represented by the formula:—

$$\begin{matrix}O\\O\end{matrix}\!\!>\!S\!<\!\begin{matrix}O—H\\O—H\end{matrix} \quad \text{or} \quad S\!<\!\begin{matrix}O—OH\\O—OH\end{matrix}.$$

The question whether the hydroxyls are in combination with sulphur or with oxygen can be answered with a fair degree of certainty by the following considerations: By replacing the two hydroxyls by chlorine the compound $Cl—SO_2—Cl$ is formed. When this compound is treated with hydrocarbons under certain conditions the chlorine is replaced by residues forming compounds called sulphones, which are represented by formulas like these, $CH_3—SO_2—C_2H_5$, $C_6H_5—SO_2—C_6H_5$. By reduction these compounds lose all their oxygen and are converted into sulphides, of which the following are examples:—

$$CH_3—S—C_2H_5, \quad C_6H_5—S—C_6H_5.$$

It cannot be doubted that in the sulphides the hydrocarbon residues are in combination with sulphur. When these sulphides are oxidized they are transformed into the sulphones. It appears, therefore, that in the compound $Cl—SO_2—Cl$, the two chlorine atoms are in combination

with the sulphur, and from this the conclusion appears to be justified that in sulphuric acid the two hydroxyls are in combination with sulphur. This leads to the formula

$$O{=}\overset{\overset{\displaystyle O{-}H}{|}}{\underset{\underset{\displaystyle O{-}H}{|}}{S}}{=}O,$$

in which the sulphur is represented as sexivalent. As between this formula and this

$$\begin{matrix}O\\|\\O\end{matrix}{>}S{<}\begin{matrix}OH\\ \\OH\end{matrix},$$

in which the sulphur is represented as quadrivalent, we have no means of deciding. The fact that sulphur appears to be sexivalent towards oxygen, as shown in the compound SO_3, makes the formula for sulphuric acid, in which the sulphur is represented as sexivalent, the most probable.

The simplest view in regard to sulphuric acid is that it is derived from the maximum hydroxide $S(OH)_6$ by elimination of water. The stable form of the acid is that in which two atoms of hydrogen are contained. On the other hand, there are a number of salts of sulphuric acid known which are derived from a more complicated acid than ordinary sulphuric acid. Examples are the following: $K_3HS_2O_8$, $K_4H_2S_3O_{12}$, and $KH_3S_2O_8$. The first and third may be regarded as derived from the acid $S_2O_4(OH)_4$, the second from an acid $S_3O_6(OH)_6$. The first acid is related to the maximum hydroxide of sulphur, as shown in this formula:—

$$_2(HO)OS{<}\begin{matrix}O\\ \\O\end{matrix}{>}SO(OH)_2.$$

If the hexahydroxide loses one molecule of water the result is a compound $SO(OH)_4$. From this the above acid may be formed as represented by this formula:—

$$_2(HO)OS{<}\begin{matrix}O|H & HO|\\ \hline O|H & HO|\end{matrix}{>}SO(OH)_2.$$

The relation between sulphurous and sulphuric acids is similar to that between formic and carbonic acids, as is shown by the formulas here given:—

16

$$C\begin{cases}H\\OH\\O\end{cases}\qquad C\begin{cases}OH\\OH\\O\end{cases}\qquad S\begin{cases}H\\OH\\O_2\end{cases}\qquad S\begin{cases}OH\\OH\\O_2\end{cases}$$

Formic acid. Carbonic acid. Sulphurous acid. Sulphuric acid.

Pyrosulphuric Acid, $H_2S_2O_7$.—Pyrosulphuric acid is formed from sulphuric acid by the abstraction of one molecule of water from two molecules of the acid:—

$$\left.\begin{array}{l}SO_2\begin{cases}OH\\OH\end{cases}\\SO_2\begin{cases}OH\\OH\end{cases}\end{array}\right\}-H_2O=\begin{array}{l}SO_2\begin{cases}HO\\ \end{cases}\\ \qquad\rangle O\\SO_2\begin{cases} \\HO\end{cases}\end{array}.$$

2 mol. sulphuric acid. Pyrosulphuric acid.

Of course, the groups SO_2 contained in this compound must be regarded as having the same constitution as in sulphuric acid.

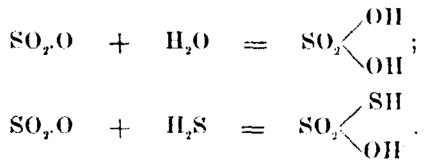
Thiosulphuric Acid, $H_2S_2O_3$.—This acid is usually considered as sulphuric acid in which one of the hydroxyl groups has been replaced by the group SH, thus:—

$$SO_2\begin{cases}OH\\OH\end{cases}\qquad SO_2\begin{cases}SH\\OH\end{cases}.$$

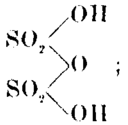
Sulphuric acid. Thiosulphuric acid.

This formula is rendered probable by the fact that the acid can be obtained from sulphuric acid by treating the latter with phosphorus sulphide. The action of the latter reagent consists in replacing oxygen by sulphur. And the oxygen of the hydroxyl group is, in general, more susceptible to the influence of reagents than that contained in the group SO_2.

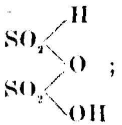
Further, thiosulphuric acid is obtained by allowing hydrogen sulphide to act upon sulphur trioxide, just as sulphuric acid is obtained by allowing water to act upon sulphur trioxide:



Dithionic Acid, $H_2S_2O_6$, is considered as related to pyrosulphuric acid, thus:—

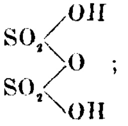


Pyrosulphuric acid.

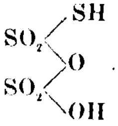


Dithionic acid.

Trithionic Acid, $H_2S_3O_6$, may be considered as derived from pyrosulphuric acid in the same way that thiosulphuric acid is derived from sulphuric acid, thus:—

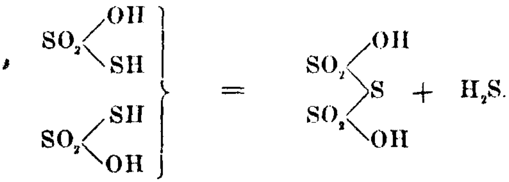


Pyrosulphuric acid.



Trithionic acid.

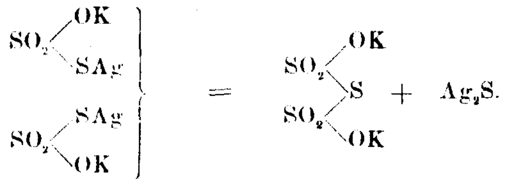
Or, it may be that trithionic acid has this constitution—



2 mol. Thiosulphuric acid. Trithionic acid.

This view finds some support in the fact that trithionates are formed when double salts of thiosulphuric acid are boiled with water. The reaction takes place according to this equation:—

$$2AgKS_2O_3 = Ag_2S + K_2S_3O_6.$$



When potassium trithionate is boiled with potassium sulphide, potassium thiosulphate is formed:—

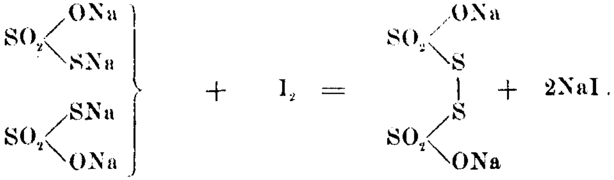
$$K_2S_3O_6 + K_2S = 2K_2S_2O_3.$$

This reaction also indicates an intimate relation between thiosulphuric and trithionic acids.

Tetrathionic Acid, $H_2S_4O_6$, is obtained by the action of iodine on sodium thiosulphate, thus:—

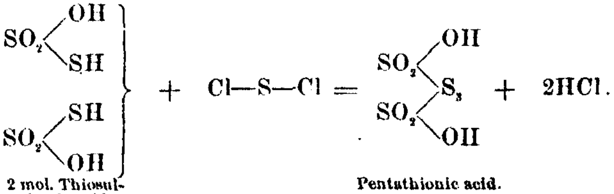
$$\left.\begin{array}{l}Na_2S_2O_3\\ Na_2S_2O_3\end{array}\right\} + I_2 = \left.\begin{array}{l}NaS_2O_3\\ NaS_2O_3\end{array}\right> + 2NaI.$$

2 mol. Sodium thiosulphate. Sodium tetrathionate.



Hence, the formula of the acid from which the latter salt is derived is accepted for tetrathionic acid.

Pentathionic Acid, $H_2S_5O_6$, is obtained by treating barium thiosulphate with sulphur dichloride, SCl_2. The latter compound has the constitution Cl—S—Cl; consequently, the reaction is most readily interpreted as follows:—



2 mol. Thiosulphuric acid. Pentathionic acid.

The corresponding acids of selenium and tellurium, as far as they are known, are represented by similar formulas, except selenious acid, which appears to be symmetrical as represented in the formula

$$O{=}Se\begin{matrix}/O{-}H\\ \backslash O{-}H\end{matrix}.$$

Compounds of Nitrogen with Oxygen, and with Oxygen and Hydrogen.—Nitrogen forms with oxygen the following compounds:—

N_2O,	nitrous oxide or nitrogen monoxide.
NO or N_2O_2,	nitric oxide.
N_2O_3,	nitrogen trioxide.
NO_2 or N_2O_4,	nitrogen peroxide.
N_2O_5,	nitrogen pentoxide.

Practically nothing is known about the arrangement of the atoms in these compounds.

Nitrous oxide is usually represented by the formula

$$\begin{matrix}N{=}N\\ \backslash\,/\\ O\end{matrix}.$$

Possibly it is analogous to chlorine monoxide Cl_2O in which the chlorine is regarded as univalent. The formula above given is not an expression of any fact known to us, except the general one that nitrogen frequently acts as a trivalent element, and rarely, if ever, as a univalent element.

If nitrogen is trivalent, it is plain that nitric oxide is unsaturated. The ease with which it takes up oxygen and chlorine is in accordance with the view that it is unsaturated.

There is little if any experimental evidence in regard to the constitution of nitrous and nitric acids except of a general kind. Nitrous acid probably contains hydroxyl, and its constitution is expressed by the formula $O{=}N{-}O{-}H$ in which the nitrogen is trivalent. The acid may be regarded as derived from the hydroxide $N(OH)_3$ by loss of one molecule of water, as represented thus:—

$$N\begin{cases}OH\\OH\\OH\end{cases} = N\begin{cases}O\\ \\OH\end{cases} + H_2O.$$

In the same way nitric acid is regarded as derived from the maximum hydroxide, $N(OH)_5$, as represented thus:—

$$N\begin{cases} OH \\ OH \\ OH \\ OH \\ OH \end{cases} = N\begin{cases} O \\ O \\ OH \end{cases} + 2H_2O.$$

While most salts of nitric acid are derived from the acid $HO.NO_2$, there are some which can only be explained on the assumption that they are derived from the acid $N\begin{cases} O \\ OH \\ OH \\ OH \end{cases}$, and the maximum hydroxide or normal acid. The probabilities for ordinary nitric acid are decidedly in favor of the formula in which the nitrogen is represented as quinquivalent.

Hydroxylamine, H_3NO.—This substance conducts itself in many respects like ammonia, and hence is regarded as a substituted ammonia. It is probable that its constitution is properly expressed by the formula $N\begin{cases} H \\ H \\ OH \end{cases}$. The formation of the aldoximes and acetoximes by treating aldehydes and acetones with hydroxylamine is fairly strong evidence in favor of the view that hydroxylamine contains hydroxyl, for these products contain hydroxyl, as has already been stated.

Compounds of Phosphorus with Oxygen, and with Oxygen and Hydrogen.—Phosphorus forms two oxides, viz:—

P_2O_3,	phosphorus trioxide.
P_2O_5,	phosphorus pentoxide.

In the former the phosphorus is regarded as trivalent, and in the latter as quinquivalent.

There are several acids of phosphorus, viz:—

H_3PO_2,	hypophosphorous acid.
H_3PO_3,	phosphorous acid.
H_3PO_4,	phosphoric acid.
$H_4P_2O_7$,	pyrophosphoric acid.
HPO_3,	metaphosphoric acid.

Hypophosphorous Acid, H_3PO_2, is monobasic, and hence only one hydroxyl group is assumed as present in its molecule. This gives the formula $H_2PO.OH$ or

$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{O{=}P{-}O{-}H} \\ | \\ \mathrm{H} \end{array}$$

in which the phosphorus atom is quinquivalent.

Phosphorous Acid, H_3PO_3.—In regard to the constitution of this acid, two views are held. According to the first, the formula of the acid is $P\begin{cases} OH \\ OH \\ OH \end{cases}$, the phosphorus being trivalent. According to the second, the formula is

$$\begin{array}{c} \mathrm{O{-}H} \\ | \\ \mathrm{O{=}P{-}H} \\ | \\ \mathrm{O{-}H} \end{array}$$

, the phosphorus being quinquivalent.

If the former formula is correct, the acid ought to be tribasic. In most of its salts, however, it is only dibasic. Still, ethereal salts are known which are evidently derived from a tribasic acid, as, for instance, $PO_3(C_2H_5)_3$; and it has, further, recently been shown that a salt of the acid exists in which there are three atoms of a univalent metal to the molecule. These facts lead to the formula $P(OH)_3$. The fact, also, that phosphorous acid is produced by simply treating phosphorus trichloride with water, is in accordance with this formula. We have

$$P\begin{cases} Cl \\ Cl \\ Cl \end{cases} + \begin{matrix} H\,HO \\ H\,HO \\ H\,HO \end{matrix} = P\begin{cases} OH \\ OH \\ OH \end{cases} + 3HCl.$$

On the other hand, the following facts speak for the formula

$$\begin{array}{c} \mathrm{O{-}H} \\ | \\ \mathrm{O{=}P{-}H} \\ | \\ \mathrm{O{-}H} \end{array}$$

:—

When benzene is treated with phosphorus trichloride, under appropriate conditions, the following reaction takes place :—

$$PCl_3 + C_6H_6 = PCl_2(C_6H_5) + HCl.$$

When the main product, phosphenyl chloride, is treated, with water, the chlorine is eliminated, and a compound of the composition $PO_2H_2(C_6H_5)$ is formed. The formula of this compound may be either

$$1,\ P\begin{cases} OH \\ OH \\ C_6H_5 \end{cases};\quad \text{or } 2,\quad \begin{array}{c} O-H \\ | \\ O{=}P-H \\ | \\ C_6H_5 \end{array}$$

If the latter is the formula, then we may conclude that the constitution of phosphorous acid is similar, *i. e.*,

$$\begin{array}{c} O-H \\ | \\ O{=}P-H \\ | \\ O-H \end{array}.$$

If formula 1 is correct, then, by the action of phosphorus pentachloride upon the compound, the following reaction ought to take place:—

$$\text{I. } P(OH)_2C_6H_5 + 2PCl_5 = PCl_2(C_6H_5) + 2(POCl_3) + 2HCl.$$

If, however, formula 2 is correct, then, under the same conditions, the following reaction would take place:—

$$\text{II. } OPH(OH)C_6H_5 + 2PCl_5 = OPCl_2(C_6H_5) + POCl_3 + PCl_3 + 2HCl.$$

In the former case, phosphenyl chloride, $PCl_2(C_6H_5)$, would be formed; in the latter, phosphenyl oxychloride, $POCl_2(C_6H_5)$. Direct experiments showed that phosphenyl oxychloride, phosphorus oxychloride, and phosphorus trichloride are formed, and consequently the formula $OPH\ (OH)C_6H_5$ appears to be correct; and phosphorous acid by analogy is $OPH(OH)_2$ or $\begin{array}{c} O-H \\ | \\ O{=}P-H \\ | \\ O-H \end{array}$.

The evidence in regard to the constitution of phosphorous acid is conflicting.

Phosphoric Acid, H_3PO_4.—This acid is tribasic, and hence three hydroxyl groups are assumed to be present

in it. From this the formula $PO(OH)_3$ follows directly. The question still remains whether the phosphorus is quinquivalent or trivalent in the acid. In the former case, the formula would be $O{=}P{\lt}\begin{smallmatrix}OH\\OH\\OH\end{smallmatrix}$; in the latter, $P{\lt}\begin{smallmatrix}O-OH\\OH\\OH\end{smallmatrix}$. Phosphoric acid is obtained by treating phosphorus oxychloride with water. If the oxychloride is $O{=}P{\lt}\begin{smallmatrix}Cl\\Cl\\Cl\end{smallmatrix}$, then we should expect phosphoric acid to have the first of the two formulas given. If the oxychloride is $P{\lt}\begin{smallmatrix}O-Cl\\Cl\\Cl\end{smallmatrix}$, then the acid has probably the latter of the two formulas given. The formulas $O{=}P{\lt}\begin{smallmatrix}OH\\OH\\OH\end{smallmatrix}$ and $O{=}P{\lt}\begin{smallmatrix}Cl\\Cl\\Cl\end{smallmatrix}$ are usually accepted, though without positive proofs of their correctness. Just as the acids of sulphur, nitrogen, and chlorine are best understood if regarded as derived from hydroxides, so phosphoric acid is to be regarded as derived from the maximum hydroxide $P(OH)_5$. The change necessary is represented in the equation:—

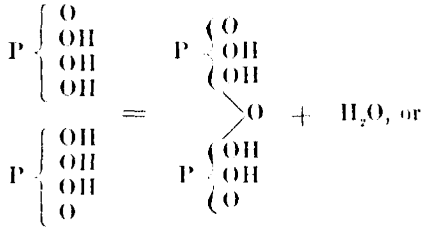
$$P(OH)_5 \quad = \quad PO(OH)_3 \quad + \quad H_2O, \text{ or}$$

$$P\left\{\begin{matrix}OH\\OH\\OH\\OH\\OH\end{matrix}\right. \quad = \quad P\left\{\begin{matrix}O\\OH\\OH\\OH\end{matrix}\right. \quad + \quad H_2O\,.$$

The maximum hydroxide or normal acid of phosphorus breaks down by loss of water until a compound is obtained in which the number of hydrogen atoms present corre-

sponds to the hydrogen valency of phosphorus. By similar processes pyrophosphoric and metaphosphoric acids are obtained from the ordinary acid.

The formation of *pyrophosphoric acid* is represented thus:—



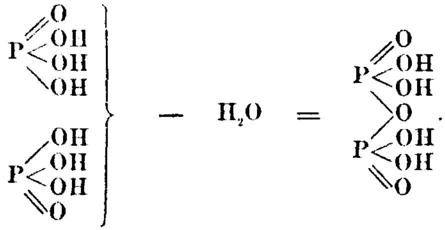
$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

The relations between hypophosphorous, phosphorous, and phosphoric acids are apparently like those between formic and carbonic acids, and those between sulphurous and sulphuric acids:—

$$O{=}P\begin{cases}H\\H\\OH\end{cases} \qquad O{=}P\begin{cases}H\\OH\\OH\end{cases} \qquad O{=}P\begin{cases}OH\\OH\\OH\end{cases}$$

Hypophosphorous Acid. Phosphorous Acid. Phosphoric Acid.

Pyrophosphoric Acid, $H_4P_2O_7$.—This is a partial anhydride of phosphoric acid formed by abstracting one molecule of water from two molecules of the acid, thus:—



2 mol. Phosphoric acid. Pyrophosphoric acid.

The constitution is readily understood by the aid of the general remarks on the subject of anhydrides.

Metaphosphoric Acid, HPO_3.—The composition of this acid is similar to that of nitric acid, HNO_3. It is, like pyrophosphoric acid, a partial anhydride of phosphoric acid, formed by abstracting one molecule of water from one molecule of the acid, thus:—

$$PO\begin{cases}OH\\OH\\OH\end{cases} - H_2O = PO_2—OH.$$

Phosphoric acid. Metaphosphoric acid.

The formation of *metaphosphoric acid* from ordinary phosphoric acid is represented thus:—

$$H_3PO_4 = HPO_3 + H_2O, \text{ or}$$

$$P\begin{cases}O\\OH\\OH\\OH\end{cases} = P\begin{cases}O\\O\\OH\end{cases} + H_2O.$$

Metaphosphoric acid bears the same relation to phosphorus that nitric acid bears to nitrogen.

Arsenic, antimony, and bismuth form compounds analogous to those of phosphorus here described. Much that has been said in regard to the latter probably holds good for the former.

Compounds of Boron with Oxygen and with Oxygen and Hydrogen.—Boron forms only one oxide, viz., B_2O_3, known as boron trioxide. The acid to which it corresponds is the maximum hydroxide or normal acid, $B(OH)_3$. When normal boric acid, $B(OH)_3$, is heated for some time at 100°, it loses a molecule of water, and the compound BO_2H is formed thus:—

$$B\begin{cases}OH\\OH\\OH\end{cases} = BO—OH + H_2O.$$

When this compound is heated to a much higher temperature it is converted into the oxide, B_2O_3, thus:—

$$\left.\begin{matrix}BO—OH\\BO—OH\end{matrix}\right\} = \begin{matrix}BO\\BO\end{matrix}\!\!>O + H_2O.$$

Other forms of boric acid are obtained by similar processes. Thus, the acid from which the most common salt of boric acid, borax, is derived has the formula $H_2B_4O_7$. Its relation to normal boric acid is indicated by this equation:—

$$4B(OH)_3 = H_2B_4O_7 + 5H_2O, \text{ or structurally,}$$

$$\begin{array}{l} B\begin{cases}OH\\OH\\OH\end{cases} \\ B\begin{cases}OH\\OH\\OH\end{cases} \\ B\begin{cases}OH\\OH\\OH\end{cases} \\ B\begin{cases}OH\\OH\\OH\end{cases} \end{array} = \begin{array}{l} B\begin{cases}O\\ \ \end{cases} \\ \qquad \rangle O \\ B\begin{cases}OH\\ \ \end{cases} \\ \qquad \rangle O \\ B\begin{cases}OH\\ \ \end{cases} \\ \qquad \rangle O \\ B\begin{cases}O\\ \ \end{cases} \end{array} + 5H_2O$$

Compounds of Silicon with Oxygen and with Oxygen and Hydrogen.—Silicon bears a close analogy to carbon in some respects. It usually acts as a quadrivalent element, as is seen in the compounds SiH_4, SCl_4, SiO_2, etc. When the chloride is treated with water, we should expect as a product $Si(OH)_4$, which may be considered as normal silicic acid. It appears to be possible to obtain this acid, but it is very unstable. It loses water easily, and yields an acid, SiO_3H_2, thus:—

$$Si(OH)_4 = SiO_3H_2 + H_2O.$$

This compound is usually called silicic acid, as many of the silicates are derived from it.

If heated, this acid yields complicated polysilicic acids. They are formed by the union of two or more molecules of silicic acid and the abstraction of varying amounts of water. Examples of such polysilicic acids are:—

$$Si_2O_3(OH)_2,\ Si_3O_4(OH)_4,\ Si_3O_5(OH)_2,\ Si_4O_7(OH)_2, \text{ etc.}$$

Some of them are found in nature, as opal, hydrophane, etc. The final product of the action of heat on silicic acid is silicon dioxide, SiO_2.

General Remarks on the Relations of ordinary Acids to the so-called Normal Acids.—In studying the common inorganic acids one cannot fail to be struck by the relations that exist between the various acids formed by each element and the hydroxides of the element; and although in many cases the hydroxides from which the acids appear to be derived are either unknown or extremely unstable, there are, nevertheless, many facts which speak in favor of the reality of these relations. To repeat briefly, the view held is that the acids are all derived from hydroxides of the elements. The hydroxides which an element can form generally correspond to the oxides; their composition being determined by the oxygen valency of the element. Thus, the hypothetical hydroxides of the members of the nitrogen family have the general formulas $M(OH)_3$ and $M(OH)_5$. The general tendency on the part of the hydroxides is to give up water enough to reduce the number of hydrogen atoms in the molecule to that which corresponds to the hydrogen valency of the group. Sometimes this goes further, as is seen in the case of carbon and nitrogen, the acids of which contain two atoms and one atom of hydrogen respectively. Both of these elements, it will be observed, belong in the first series in which oxygen and fluorine belong. The members of the next series obey the law, as well as the members of the fourth and sixth short periods.

The hydroxides from which the acids are derived are called *normal acids*. Thus, normal carbonic acid is $C(OH)_4$; normal sulphuric acid $S(OH)_6$; normal silicic acid $Si(OH)_4$; normal nitric acid $N(OH)_5$; normal periodic acid $I(OH)_7$, etc. In very few of these normal acids are all the hydrogen atoms replaceable by metals. Salts of the order $S(OM)_6$, $N(OM)_5$, etc., are not known except in the case of a few normal acids. Many salts of sulphuric acid, however, appear to be formed by the replacement of two atoms of hydrogen in the normal acid. The remaining hydroxyls are commonly represented as "water of crystallization," and the acid from which the salts are derived is represented by the formula $SO_2\langle{OH \atop OH}$. We have no means of deciding whether that part of the compound which is represented as water of crystallization is

properly represented in this way, and we have just as much right to represent it, or a part of it, as present in the form of hydroxyl in the compound. Thus, for example, a sulphate with two molecules of water of crystallization may with equal right be represented thus, $S\begin{cases}(OH)_4\\(OM)_2\end{cases}$, which indicates, of course, the same composition as the common formula, $SO_2(OM)_2 + 2H_2O$. Further, there are many double salts of sulphuric acid which cannot be explained at all by the usual method, but which are easily understood, if they be regarded as derived from the acid $SO(OH)_4$. Many sulphates, too, give up a part of their so-called water of crystallization less readily than the rest. The formation of the salt which is commonly called the double sulphate of magnesium and potassium, $(SO_4)_2MgK_2$, can be explained by assuming that magnesium sulphate has the formula $SO\begin{cases}(OH)_2\\ O \\ O\end{cases}\!\!>Mg$. The action of potassium sulphate upon it would then be represented thus:—

$$SO\begin{cases}(OH)_2\\ O\\ O\end{cases}\!\!>Mg + SO\begin{cases}(OH)_2\\(OK)_2\end{cases} = (MgO_2)SO\!<\!\begin{matrix}O\\O\end{matrix}\!>\!SO(OK)_2 + 2H_2O.$$

That all the hydrogen in the normal acids is not replaced by metals is not entirely without analogy. Ordinary phosphoric acid which in all probability contains three hydroxyl groups, is only dibasic towards sodium. The periodates, which until recently have been regarded as inexplicable, are easily understood if referred to the normal acid $I(OH)_7$. Most of the periodates are derived from the acid $IO(OH)_5$, which is $I(OH)_7—H_2O$. The sodium salt is $IO\begin{cases}(OH)_3\\(ONa)_2\end{cases}$, which is analogous to sodium phosphate $PO\begin{cases}(OH)\\(ONa)_2\end{cases}$. The crystallized acid has the composition $IO(OH)_5$, usually represented by the formula $HIO_4 + 2H_2O$. The silver salt is $IO(OAg)_5$. Many periodates of more complicated composition are known, but they can all be understood on the assumption that they are derived from acids which bear to ordinary periodic acid relations similar to those which pyrophos-

phoric acid bears to ordinary phosphoric acid, and the polysilicic acid to ordinary silicic acid.

Salts.—The constitution of the most important acids having been explained, that of the salts, in general, requires no special consideration, for the salts are, as a rule, very simple derivatives of the acids. There are a few metals and groups, however, which have the property of forming peculiar salts, and these require brief consideration.

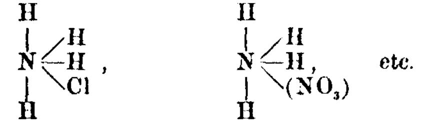
Ammonium Salts.—When ammonia, NH_3, acts upon an acid, a salt is formed by direct addition, thus:—

$$NH_3 + HCl = (NH_4)Cl \quad \text{Ammonium chloride.}$$

$$NH_3 + HNO_3 = (NH_4)NO_3 \quad \text{Ammonium nitrate.}$$

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4. \quad \text{Ammonium sulphate.}$$

The salts thus formed are similar to the salts of potassium, sodium, etc., KCl, KNO_3, K_2SO_4, etc. They conduct themselves like true metallic salts. Hence, that part of these compounds which corresponds to the metal in metallic salts, viz., the group NH_4, plays the part of a metal, and to it the name *ammonium* is given. Accordingly, the salts are called ammonium salts. These have been referred to incidentally under the head of valency. It was shown that in them the nitrogen is probably quinquivalent. The formulas of the above salts are, accordingly:—



Salts of Copper and Mercury.—Copper and mercury form two series of salts, of which the following are examples:—

CuCl	$CuCl_2$	HgCl	$HgCl_2$
CuBr	$CuBr_2$	$HgNO_3$	$Hg(NO_3)_2$
		Hg_2SO_4	$HgSO_4$

The specific gravity of the vapors of the two chlorides of mercury leads to the formulas $HgCl$ and $HgCl_2$. According to these formulas, mercury is bivalent, and the compound $HgCl$ is unsaturated. It has been suggested, however, that the formula of the chloride $HgCl$ in the solid condition is Hg_2Cl_2, and that it has the constitution $\begin{array}{c} HgCl \\ | \\ HgCl \end{array}$.

The group $\begin{array}{c} Hg \\ | \\ Hg \end{array}$, as well as the mercury atom itself, is bivalent, and thus the above two series of salts are explained. The same explanation is given for the corresponding salts of copper. It is impossible to decide this point with the present evidence.

A large number of compounds are known which are derived from salts of ammonium and contain copper and mercury. They seem to consist of ammonium salts, in which a portion of the hydrogen of the ammonium groups has been replaced by copper or mercury, thus:—

$$\begin{array}{l} \quad Cl \\ \quad | \\ H_3N-Hg \\ \qquad\quad | \\ H_3N-Hg \\ \quad | \\ \quad Cl \end{array}, \qquad \begin{array}{c} NO_2-ONH_2 \\ \quad\| \\ \quad Hg_2 \end{array}, \qquad ClN \left\{ \begin{array}{l} H_2 \\ Hg \end{array} \right. \text{ etc.}$$

The first of these is formed by passing dry ammonia over dry mercurous chloride Hg_2Cl_2; the second, known as dimercuryamine nitrate, or *mercurius solubilis Hahnemanni*, is the black powder which is formed by adding ammonia to a solution of mercurous nitrate; the third, mercuryamido chloride, or infusible white precipitate, is formed by adding an excess of ammonia to a solution of mercuric chloride.

Similar compounds are formed with other metals, particularly with cobalt, which furnishes a very large number of interesting substances of this kind. These are too complicated and too little understood to permit the drawing of positive conclusions concerning their constitution. Their study promises interesting results.

Salts of Iron and Chromium.—Iron and chromium form two series of salts in regard to the relations between which but little is known. In the ferrous salts the iron appears to be bivalent, while in the ferric salts it is trivalent:—

$FeCl_2$	$FeCl_3$
$Fe(NO_3)_2$	$Fe(NO_3)_3$
$FeSO_4$	$Fe_2(SO_4)_3$.

Specific gravity determinations have been made in the case of the two chlorides, and they appear to have the molecular formulas Fe_2Cl_4 and Fe_2Cl_6, but as to their constitution nothing is known.

The same general statements hold good for the two series of chromium salts.

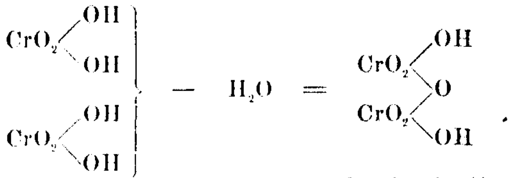
Metal Acids.—The four metals, iron, chromium, manganese, and aluminium, form hydroxides of the general formula MO.OH, which conduct themselves like weak acids, forming salts with some metals. Thus, we have AlO.OK and AlO.ONa, salts of the hydroxide AlO.OH. These are derived from the hydroxides of the general formula $M(OH)_3$ by elimination of one molecule of water, just as the common inorganic acids are derived from the normal acids.

Iron, manganese, and chromium yield acids of the general formula MO_4H_2. Thus, we have FeO_4H_2, MnO_4H_2, and CrO_4H_2. These acids are analogous to sulphuric acid, H_2SO_4, and a close resemblance is noticed between the salts of sulphuric acid and those of chromic acid, which is the best known of the three acids named.

In the absence of satisfactory evidence regarding the constitution of these acids, the only formulas which we are at all justified in using are those which have the general form $MO_2\begin{cases}OH\\OH\end{cases}$. The analogy to sulphuric makes it appear probable that they have an analogous constitution.

A very important salt of chromium is that known as potassium bichromate or pyrochromate. The formula of this salt is $Cr_2O_7K_2$. It may be regarded as the salt of an acid which is analogous to pyrosulphuric acid, and derived from chromic acid by the abstraction of water, thus:—

17*



2 mol. Chromic acid. Pyrochromic acid.

Neither chromic acid itself nor pyrochromic acid can be prepared in the free condition. The group CrO_2 does not appear to be capable of holding hydroxyl in combination, so that salts of the formula $CrO_2\begin{matrix}\diagup OH \\ \diagdown OM\end{matrix}$ are not known.

An acid of manganese furnishes salts of the general formula MnO_4M. No positive assertion can be made in regard to the constitution of this acid, except that it is monobasic, and hence probably contains one hydroxyl group. This gives the formula $MnO_3—OH$, but the group MnO_3 remains unexplained. As manganese belongs in Group VII, it is probable that this acid is analogous to perchloric and periodic acids, and, according to this view, the manganese is septivalent.

Compounds of Uranium.—In connection with the subject of bases it was mentioned that uranium forms a peculiar set of salts in which the bivalent group UO_2 is regarded as taking the place of the hydrogen of the acids. Thus, we have the following compounds, UO_2Cl_2, $UO_2(NO_3)_2$, $UO_2(SO_4)$, etc., which can be most readily explained by assuming that in them the group UO_2 acts like a bivalent metal. This is readily understood, if uranium be considered sexivalent, which would be in accordance with its position in the periodic system.

Uranium, further, forms salts of the general formula $U_2O_7M_2$, which may be regarded as derived from an acid,

$$U_2O_7H_2 = O\begin{matrix}\diagup (UO_2)OH \\ \diagdown (UO_2)OH\end{matrix},$$

that appears to be analogous to pyrosulphuric and pyrochromic acid.

CHAPTER XIII.

CONSTITUTION OF CARBON COMPOUNDS.

As has already been stated, a great deal more is known concerning the constitution of carbon compounds than of those compounds which do not contain carbon. Having considered the general constitution of the classes of compounds which are met with, it remains to study those changes which the members of the different classes undergo without losing their characteristic properties. It will be found that the compounds of carbon may be divided into a few distinct groups; that each of these groups may be referred to some fundamental substance of which all the other members of the group are to be regarded as derivatives. The principal groups are: The Marsh gas, or Methane compounds, also called Fatty compounds; the Benzene compounds, also called Aromatic compounds; the Naphthalene compounds; and the Anthracene compounds. The first two groups comprise by far the largest number of carbon compounds.

METHANE DERIVATIVES. (FATTY COMPOUNDS.)

Compounds derived from the Hydrocarbons C_nH_{2n+2}.

The constitution of methane has been discussed above (see *ante*, p. 136). It was shown that by the linking of carbon atoms to one another the possibility is given of the formation of an homologous series, the members of which differ from one another by CH_2, or a multiple of this. The following members of the series have been particularly well studied.

Methane,	CH_4.	Pentane,	C_5H_{12}.
Ethane,	C_2H_6.	Hexane,	C_6H_{14}.
Propane,	C_3H_8.	Heptane,	C_7H_{16}.
Butane,	C_4H_{10}.	Octane,	C_8H_{18}.

In speaking of substitution products it was stated that, according to the views now held concerning constitution, only one mono-substitution product of methane can exist. The same thing is true of the other substitution products of methane in which more than one substituting group is present. Further, we can conceive of only one variety of methane itself, and only one variety has ever been observed.

Derivatives of Ethane, C_2H_6.—According to the prevailing views, only one variety of this hydrocarbon can exist, and only one variety has been observed. Of its mono-substitution products, also, only one variety can exist, and only one variety has been observed.

Of the di-substitution products, however, two varieties are possible, as will be seen on comparing the following formulas:—

$$\begin{array}{ccccccc} & H & & H & & \\ & | & & | & & \\ X- & C & - & C & -X \\ & | & & | & & \\ & H & & H & & \end{array} \quad \text{and} \quad \begin{array}{ccccccc} & H & & X & & \\ & | & & | & & \\ H- & C & - & C & -X. \\ & | & & | & & \\ & H & & H & & \end{array}$$

In the first, the substituting groups are in combination with different carbon atoms: in the second, both substituting groups are in combination with the same carbon atom.

A number of compounds are known belonging to the classes of which these are the general formulas. X may represent any of the substituting groups with which we have had to deal; or the class groups CH_2OH, COH, $COOH$, etc.

The simplest of these are the dichlorine derivatives, one of which is $CHCl_2.CH_3$, and the other $CH_2Cl.CH_2Cl$. The first is called *ethylidene chloride*, the second *ethylene chloride*. The constitution of these compounds is deduced from the following facts:—

Ethylidene chloride is formed by the action of phosphorus pentachloride on aldehyde. It has been shown that an aldehyde contains the group $-\overset{H}{\overset{/}{C}}-O$. Ordinary aldehyde is $CH_3-\overset{H}{\overset{/}{C}}-O$. As in the reaction with phos-

phorus chloride, the oxygen is simply replaced by chlorine, the constitution $CH_3—CHCl_2$ follows for ethylidene chloride. It follows, further, that $CH_2Cl.CH_2Cl$ must be the formula of ethylene chloride.

Other compounds closely related to these two chlorides will be treated under the heads of ethylene, dibasic acids, etc.

Isomerism.—Two or more substances that have the same composition, but different properties, are said to be isomeric. The existence of isomeric compounds is one of the most interesting as well as important facts which we have to deal with in the field of organic chemistry. Much of the work that has been done in chemistry during the last half century has had for its immediate object the explanation of cases of isomerism. And one of the strongest arguments in favor of the general correctness of the views at present held in regard to the structure of the compounds of carbon is found in the ease with which the innumerable phenomena of isomerism are explained by them.

There are in general two ways in which compounds may contain the same elements in the same proportion by weight, and still have different properties:—

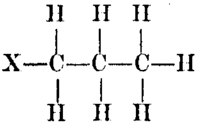
1. The atoms or groups entering into the composition of the compound may be arranged differently in the molecule. Thus there is the compound ammonium cyanate, $CN(ONH_4)$, and the isomeric compound urea $CO(NH_2)_2$. These formulas may also be written thus: $N \equiv C—O—NH_4$ and $O{=}C\begin{cases}NH_2\\NH_2\end{cases}$. Compounds which bear such relations to one another are said to be *metameric*.

2. Compounds may have the same percentage composition, but different molecular weights. Thus acetylene C_2H_2, benzene, C_6H_6, and styrene, C_8H_8, bear this relation to one another. Such compounds are said to be *polymeric*.

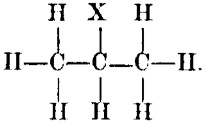
Derivatives of Propane, C_3H_8.—Propane may be regarded as a mono-substitution product of ethane, derived from the latter by replacing an atom of hydrogen by CH_3.

From what was said above, it will be seen that only one variety of propane can exist.

Under the head of substitution products, it has been shown that there are two kinds of carbon atoms, and consequently two kinds of hydrogen atoms in propane; and hence, further, that two different mono-substitution products can be obtained from this hydrocarbon. These have the general formulas:—



and

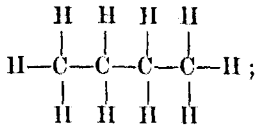


The compounds represented by the first formula are known as propyl compounds; those represented by the second formula as isopropyl or pseudopropyl compounds.

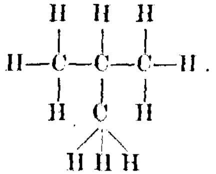
The two alcohols, normal propyl alcohol, $CH_3.CH_2.CH_2OH$, and isopropyl or pseudopropyl alcohol, $CH_3CHOH.CH_3$, are the starting-points for the preparation of the two series of isomeric propyl compounds. As the former is a primary alcohol, it follows, from what has been said concerning these alcohols, that it must contain the group CH_2OH. This can only be the case if the hydroxyl group is in combination with one of the terminal carbon atoms. Consequently, the above constitution is assigned to it. By replacing the hydroxyl by chlorine, bromine, iodine, cyanogen, etc., corresponding derivatives are obtained.

Isopropyl alcohol is obtained from acetone, and, being a secondary alcohol, contains the group $CH.OH$. Its hydroxyl is in combination with the central carbon atom of propane. By replacing the hydroxyl, chlorine, bromine, iodine, cyanogen, etc., corresponding isopropyl derivatives are obtained.

Derivatives of Butane, C_4H_{10}.—Butane may be regarded as a mono-substitution product of propane; consequently, two varieties must be possible, one of which would have the formula:—

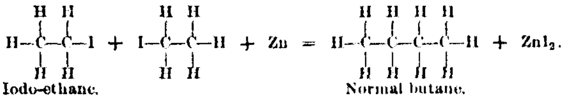
I. 

while the other would have the formula:—

II. 

As a matter of fact, two varieties of butane are known, viz., normal butane and isobutane or trimethyl-methane.* The former has the constitution represented by formula I., above; the latter that represented by formula II.

Experimental Evidence.—The evidence in favor of the formula of normal butane is the same in nature as that given for ethane. The compound is formed by the action of zinc or sodium on iodo ethane, according to the equation:—



Iodo-ethane. Normal butane.

Of course it is here assumed that the formula of iodo-ethane is known, but good grounds for this assumption

* The simplest names for the members of the methane series of hydrocarbons are those in which the members are all regarded as derivatives of methane. Thus, ethane is called methyl-methane, $C\left\{\begin{matrix}CH_3\\H\\H\\H\end{matrix}\right.$; propane is ethyl-methane, $C\left\{\begin{matrix}C_2H_5\\H\\H\\H\end{matrix}\right.$; normal butane is propyl-methane, $C\left\{\begin{matrix}C_3H_7\\H\\H\\H\end{matrix}\right.$; isobutane is trimethyl-methane $C\left\{\begin{matrix}CH_3\\CH_3\\CH_3\\H\end{matrix}\right.$, etc.

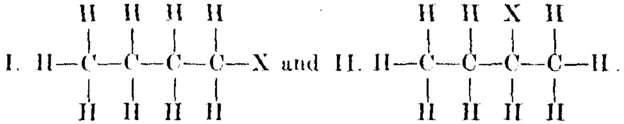
have been presented. Starting with this formula, we are led very easily to the above formula of normal butane.

Trimethylmethane is obtained from pseudobutyl iodide, the constitution of which is known to be

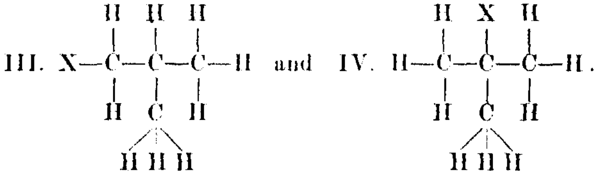
$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big\rangle CI—CH_3 .$$

When the iodine is replaced by hydrogen, the hydrocarbon is the product. (See Pseudobutyl Alcohol.)

Of normal butane, two kinds of simple substitution products are possible of the general formulas:—



Of trimethylmethane, there are also two kinds possible, of the formulas:—



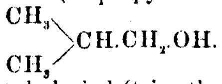
Representatives of all four kinds of substitution products are known. The principal of these are the alcohols.

1. Normal butyl alcohol (propyl carbinol),*

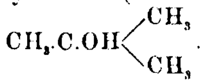
$$CH_3.CH_2.CH_2.CH_2.OH.$$

* The simplest names for the alcohols are those according to which they are regarded as derivatives of methyl alcohol or carbinol. Thus ethyl alcohol is methyl carbinol, $C\left\{\begin{matrix} CH_3 \\ H \\ H \\ OH \end{matrix}\right.$; normal propyl alcohol is ethyl carbinol, $C\left\{\begin{matrix} C_2H_5 \\ H \\ H \\ OH \end{matrix}\right.$; secondary propyl alcohol is dimethyl carbinol, $C\left\{\begin{matrix} CH_3 \\ CH_3 \\ H \end{matrix}\right.$, etc.

2. Secondary butyl alcohol (methyl-ethyl carbinol),
$$CH_3.CH.OH.CH_2.CH_3.$$
3. Isobutyl alcohol (isopropyl carbinol),



4. Tertiary butyl alcohol (trimethyl carbinol),



From each of these alcohols the corresponding chlorides, bromides, etc., can easily be obtained.

Experimental Evidence.—Normal butyl alcohol is obtained indirectly from normal butyric acid, the constitution of which is known.

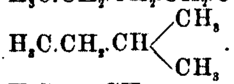
Secondary butyl alcohol is converted by oxidation into ethyl-methyl ketone, $C_2H_5—CO—CH_3$. It is, hence, a secondary alcohol, and its constitution is that expressed above.

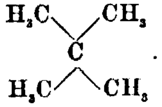
Isobutyl alcohol is converted into isobutyric acid by oxidation. The constitution of the acid is known, and hence also that of the alcohol.

Tertiary butyl alcohol is a tertiary alcohol, and hence, from what has been said regarding these alcohols, it follows that it contains the group —C—O—H. It is prepared by treating acetyl chloride, $CH_3.COCl$, with zinc methyl, $Zn(CH_3)_2$, and hence contains three methyl groups. The only formula which is in accordance with these facts is that above assigned to the alcohol.

Derivatives of Pentane, C_5H_{12}.—Three varieties of pentane are possible, according to the theory. These have the formulas:—

1. $H_3C.CH_2.CH_2.CH_2.CH_3.$

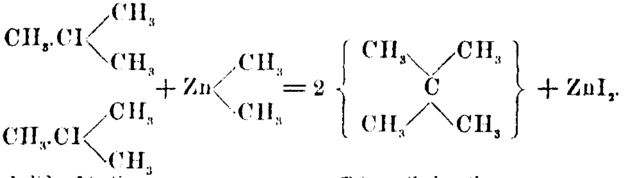
2. 

3. 

All three of these compounds are known. The first is *normal pentane;* the second is *dimethyl-ethyl methane;** and the third *tetramethyl-methane.*

Dimethyl-ethyl methane is derived from ordinary amyl alcohol, and hence has the same general constitution. The evidence for the constitution of this alcohol will be given below.

Tetramethyl-methane is derived from the iodide of tertiary butyl alcohol by the action of zinc methyl. The reaction is believed to take place as follows:—



Iodide of tertiary butyl alcohol. Tetramethyl-methane.

A great variety of substitution products can be obtained from the isomeric butanes. Theory indicates the possible existence of eight alcohols, of which seven are known. These are:—

1. Normal amyl alcohol (butyl carbinol),

$$CH_3.CH_2.CH_2.CH_2.CH_2.OH.$$

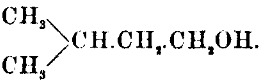
2. Methyl-propyl carbinol,

$$CH_3.CH_2.CH_2.CHOH.CH_3.$$

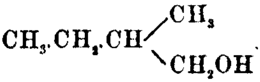
3. Diethyl carbinol,

$$CH_3.CH_2.CHOH.CH_2.CH_3.$$

4. Isoamyl alcohol (isobutyl carbinol),



5. Active amyl alcohol (secondary butyl carbinol),



6. Methyl-isopropyl carbinol,

$$CH_3.CHOH.CH\begin{cases}CH_3\\CH_3\end{cases}.$$

7. Dimethyl-ethyl carbinol,

$$CH_3.CH_2.COH\begin{cases}CH_3\\CH_3\end{cases}.$$

These alcohols form the starting-points for the preparation of corresponding substitution products.

Experimental Evidence.—Normal amyl alcohol is obtained from normal valeric acid, and yields this acid by oxidation. The constitution of the acid follows from its method of preparation. (See Normal Valeric Acid.)

Methyl-propyl carbinol yields methyl-propyl ketone, $CH_3—CO—C_3H_7$, by oxidation, and is formed by reduction of this compound.

Diethyl carbinol yields diethyl ketone, $C_2H_5—CO—C_2H_5$, by oxidation.

Secondary Butyl Carbinol.—For reasons that will be considered further on, it has been suggested that in compounds which are optically active, there is a carbon atom linked to four different kinds of atoms or groups. Such an atom is called *asymmetrical.* Now, as secondary butyl carbinol is an optically active compound, it is believed to contain an asymmetrical carbon atom. Further, it is a primary alcohol, and hence probably contains the group CH_2OH. The only formula in accordance with these facts is

$$CH_2OH—\overset{\displaystyle CH_3}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}—C_2H_5,$$

which is identical with the one above given.

Methyl-isopropyl carbinol is formed by reduction of methyl-isopropyl ketone, $CH_3—CO—CH\begin{cases}CH_3\\CH_3\end{cases}$.

Dimethyl-ethyl carbinol acts like a tertiary alcohol, and is hence believed to contain the group COH. The formula above given is the only one possible for a tertiary amyl alcohol.

Derivatives of Hexane, C_6H_{14}.—Five hexanes are possible according to the theory, and all of them are known. These are :—

1. Normal hexane, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_3$.
2. Dimethyl-propyl-methane, $CH_3.CH_2.CH_2.CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$.
3. Methyl-diethyl-methane, $CH_3.CH\left\langle\begin{matrix}CH_2.CH_3\\CH_2.CH_3\end{matrix}\right.$.
4. Di-isopropyl (Tetramethyl-ethane),
$$\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\rangle CH—CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. .$$
5. Trimethyl-ethyl-methane, $CH_3—\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}—CH_2.CH_3$.

Experimental Evidence.—Normal hexane is formed when normal propyl iodide is heated with sodium :—

$$H_3C.CH_2.CH_2I + ICH_2.CH_2.CH_3 + Na_2 =$$
$$CH_3.CH_2.CH_2.CH_2.CH_2.CH_3 + 2NaI.$$

Dimethyl-propyl methane is formed from ethyl iodide and isobutyl iodide by treating the mixture with sodium :—

$$CH_3.CH_2I + ICH_2.CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. + Na_2 =$$
$$CH_3.CH_2.CH_2.CH\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right. + 2NaI .$$

Methyl-diethyl methane is formed by treating a mixture of methyl iodide and active amyl iodide with sodium:—

$$CH_3I + \begin{array}{l} ICH_2 \\ CH_3 \end{array}\!\!>CH.CH_2.CH_3 + 2Na = \begin{array}{l} CH_3.CH_2 \\ CH_3 \end{array}\!\!>CH.CH_2.CH_3 + 2NaI .$$

Di-isopropyl (tetramethyl ethane) is formed by treating isopropyl iodide with sodium:—

$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CHI + ICH<\!\!\begin{array}{l} CH_3 \\ CH_3 \end{array} + 2Na = \begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CH—HC<\!\!\begin{array}{l} CH_3 \\ CH_3 \end{array} + 2NaI .$$

Trimethyl-ethyl methane is obtained by the action of zinc ethyl on tertiary butyl iodide:—

$$2\left\{\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CI.CH_3\right\} + Zn(C_2H_5)_2 = 2\left\{\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>C<\!\!\begin{array}{l} C_2H_5 \\ CH_3 \end{array}\right\} + ZnI_2 .$$

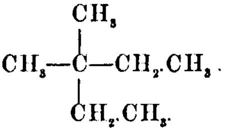
Derivatives of Heptane, C_7H_{16}.—Of the nine hydrocarbons of the formula C_7H_{16}, the existence of which is indicated by the theory, five are known up to the present:—

1. Normal heptane, $CH_3.CH_2.CH_2.CH_2.CH_2.CH_2.CH_3$.
2. Isoheptane (dimethyl-butyl methane),

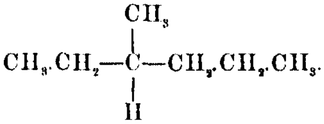
$$\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>CH.CH_2.CH_2.CH_2.CH_3 .$$

3. Triethyl methane, $\begin{array}{l} \qquad\qquad\quad CH_2.CH_3 \\ CH_3.CH_2—\overset{|}{\underset{|}{C}}H \\ \qquad\qquad\quad CH_2.CH_3 \end{array}$.

18*

4. Dimethyl-diethyl methane, 

5. Methyl-ethyl-propyl methane,



A large number of alcohols have been prepared, and the connection between them and the heptanes established. It is unnecessary to consider them here.

CHAPTER XIV.

MONOBASIC ACIDS, $C_nH_{2n}O_2$, ETC.

THE acids of this series may be regarded as substitution products of the hydrocarbons, formed by replacing a hydrogen atom of the latter by carboxyl (COOH); or as carbonic acid, $CO\langle{}^{OH}_{OH}$, in which one of the hydroxyls has been replaced by a hydrocarbon residue, as represented in the formula $O = C\langle{}^{R}_{OH}$. The two views are identical. In most cases these acids have been prepared by converting the group CN of the cyanides of hydrocarbon residues into COOH. If the constitution of the cyanide is known, the constitution of the acid is readily deduced.

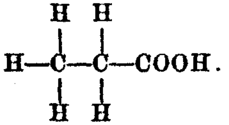
The principal members of the series are:—

Formic acid,	H.COOH.
Acetic acid,	CH_3.COOH.
Propionic acid,	C_2H_5.COOH.
Butyric acid,	C_3H_7 COOH.
Valeric acid,	C_4H_9.COOH.
Caproic acid,	C_5H_{11}.COOH.

Of formic acid and its substitution products only one variety is known.

Of acetic acid and its substitution products, also, only one variety is known.

Propionic Acid. With propionic acid the case is different. Of the acid itself only one variety is known, but of the mono-substitution products two varieties are known. The constitution of the acid is represented thus:



Now it is plain that, in this com-

pound, aside from the hydrogen of the carboxyl group; there are two kinds of hydrogen atoms—those combined with a carbon atom, which in its turn is in combination with the group CH_2, and those in combination with a carbon atom, which in its turn is in combination with two carbon atoms. The case is similar to that of propane, of which two varieties of substitution products are possible. The two possibilities are expressed by the formulas:—

$$\begin{array}{ccccc} & & H & & X \\ & & | & & | \\ H & — & C & — & C—COOH \\ & & | & & | \\ & & H & & H \end{array} \quad \text{and} \quad \begin{array}{ccccc} & & H & & H \\ & & | & & | \\ X & — & C & — & C—COOH. \\ & & | & & | \\ & & H & & H \end{array}$$

Those which have the first formula are called α-substitution products; those which have the second are called β-substitution products.* The best known representatives of these two classes are two lactic acids. The lactic acids are derived from propionic acid by substituting hydroxyl for a hydrogen atom. β-iodo-propionic acid is converted into hydracrylic acid (one of the lactic acids) when boiled with water. The change consists in substituting hydroxyl (OH) for the iodine. Hydracrylic acid is formed from ethylene, which will be shown to have the formula $\begin{array}{c} CH_2 \\ | \\ CH_2 \end{array}$ or $\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array}$ by the following reactions:—

Ethylene takes up hypochlorous acid, HClO, and becomes $\begin{array}{c} CH_2OH \\ | \\ CH_2Cl \end{array}$, ethylene-chlorhydrin. This product is easily transformed into ethylene-cyanhydrin, $\begin{array}{c} CH_2OH \\ | \\ CH_2.CN \end{array}$, and this

* In naming the isomeric substitution products of the acids, that one in which the substituting atom or group takes the place of a hydrogen in combination with the carbon atom with which the carboxyl is united is designated as the α-product; that one in which a hydrogen of the next carbon is replaced is called the β-product, etc. In the case of an acid of the formula $H_3C.CH_2.CH_2.COOH$, for example, the α-product is represented by the formula $H_3C.CH_2CHXCOOH$, the β-product by $H_3C.CHXCH_2.COOH$, and the γ-product by $H_2XC.CH_2.CH.COOH$.

in turn into hydracrylic acid, $\begin{array}{l} CH_2OH \\ | \\ CH_2.COOH \end{array}$.

The constitution of hydracrylic acid is easily deduced from these reactions. As *β-iodo-propionic* acid is converted into hydracrylic acid by boiling water, it further follows that β-iodo-propionic acid has the constitution—

$$\begin{array}{l} CH_2I \\ | \\ CH_2COOH \end{array} \quad \text{or} \quad \begin{array}{c} \quad\ H \quad H \\ \quad\ | \quad\ | \\ I—C—C—COOH \\ \quad\ | \quad\ | \\ \quad\ H \quad H \end{array}.$$

All mono-substitution-products of propionic acid which have been converted into or formed by simple reactions from β-iodo-propionic acid are called β-compounds, and they are all assumed to have the same general constitution.

Having determined the constitution of the β-compounds, that of the α-compounds follows. It must be represented by the other possible general formula

Butyric Acids.—Two acids of the formula $C_3H_7.COOH$ are theoretically possible and two are known. These are *normal butyric acid*, $CH_3.CH_2.CH_2.COOH$, and *isobutyric acid*, $\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!>\!CH.COOH$.

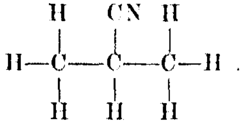
Experimental Evidence.—Normal butyric acid is prepared by introducing the group C_2H_5 into acetic acid by a reaction the essential part of which is represented by the equation:—

$$CH_2Na.COOH + C_2H_5I = C_2H_5.CH_2.COOH + NaI.$$

Further, by reduction, normal butyric acid yields one of the two possible primary butyl alcohols. It has been shown that the other possible primary butyl alcohol is not a derivative of normal butane, consequently normal butyric acid must have a constitution like that of normal butane, and it has the formula above assigned to it.

Isobutyric acid is obtained from isopropyl cyanide,

and this has been shown to have the constitution



From this the above formula follows for isobutyric acid.

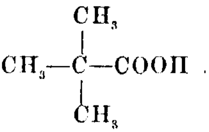
Valeric Acid.—Four acids of the formula $C_5H_{10}O_2$ are known. These are :—

1. Normal valeric acid, $CH_3.CH_2.CH_2.CH_2.CO.OH$.

2. Isovaleric acid, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2.COOH$.

3. Hydrotiglic acid, Methylethylacetic acid, $\begin{matrix}CH_3.CH_2\\CH_3\end{matrix}\!\!>CH.CO.OH$.

4. Trimethylacetic acid,



Evidence.—*Normal valeric acid* can be prepared indirectly from normal butyl alcohol by three reactions :—

$$CH_3.CH_2.CH_2.CH_2OH + HCl = CH_3.CH_2.CH_2.CH_2Cl + H_2O.$$

$$CH_3.CH_2.CH_2.CH_2Cl + KCN = CH_3.CH_2.CH_2.CH_2CN + KCl.$$

$$CH_3.CH_2.CH_2.CH_2CN + 2H_2O = CH_3.CH_2.CH_2.CH_2.COOH + NH_3.$$

Isovaleric acid is formed from isobutyl iodide, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CH.CH_2I$, by making the cyanide and converting the cyanogen group into carboxyl.

Trimethylacetic acid is made from tertiary butyl iodide

$$\begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}I \\ | \\ CH_3 \end{array}, \text{ through the cyanide.}$$

Caproic Acids.—Six acids of the formula $C_6H_{12}O_2$ are known. These are:—

1. Normal caproic acid, $CH_3.CH_2.CH_2.CH_2.CH_2.COOH$.
2. Isobutylacetic acid, $\begin{array}{l} CH_3 \\ CH_3 \end{array}\rangle CH.CH_2.CH_2.COOH$.
3. Diethylacetic acid, $\begin{array}{l} CH_3.CH_2 \\ CH_3.CH_2 \end{array}\rangle CH.COOH$.
4. Methylpropylacetic acid, $\begin{array}{r} CH_3 \\ CH_3.CH_2.CH_2 \end{array}\rangle CH.COOH$.
5. Dimethylethylacetic acid, $\begin{array}{l} CH_3 \\ CH_3 \end{array}\rangle C \langle \begin{array}{l} CH_2CH_3 \\ COOH \end{array}$.
6. Isocaproic acid,
   Methylisopropylacetic acid, $\begin{array}{r} CH_3 \\ (CH_3)_2CH \end{array}\rangle CH.COOH$.

Experimental Evidence.—*Normal caproic acid* is obtained by oxidizing normal hexyl alcohol, and from normal amyl iodide through the cyanide.

Isobutylacetic acid has been prepared by introducing isobutyl into acetic acid:—

$$\begin{array}{c} CH_2Na \\ | \\ COOH \end{array} + \begin{array}{l} CH_3 \\ CH_3 \end{array}\rangle CH.CH_2I = \begin{array}{l} CH_3 \\ CH_3 \end{array}\rangle CH.CH_2.CH_2.COOH + NaI.$$

Diethylacetic acid is obtained by introducing two ethyl groups into acetic acid:—

$$\begin{matrix} CHNa_2 \\ | \\ COOH \end{matrix} + 2C_2H_5I = \begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!>\!CH.CO.OH + 2NaI.$$

Dimethylethylacetic acid is prepared indirectly from dimethylethyl carbinol, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} C_2H_5 \\ OH \end{matrix}$, by introducing iodine in the place of hydroxyl, then substituting the cyanogen group for the iodine and converting the cyanogen into carboxyl.

The other acids of this series are not very well known. By the aid of the foregoing examples, the method of determining the constitution of the acids will be readily understood.

Aldehydes.—Corresponding to every primary alcohol and to every acid an aldehyde is possible. The constitution of each of these aldehydes is given if the constitution of the alcohol or of the acid from which it is obtained is known.

The aldehydes are produced from the primary alcohols by partial oxidation; and from the acids by subjecting a mixture of a salt of the acid and a salt of formic acid to dry distillation.

Acetones or Ketones.—The ketones are obtained by distilling mixtures of two acids. If the constitution of the acid or acids is known, that of the ketone obtained in each case is also known.

Diacid Alcohols, $C_nH_{2n+2}O_2$.—The alcohols thus far considered are the simplest. They act like mon-acid bases, such as potassium and sodium hydroxides, KOH and NaOH, etc. Corresponding to diacid bases there are also diacid alcohols. The simplest substance of this kind known is *ethylene alcohol* or *glycol*, $C_2H_6O_2$. This substance is found to act like an alcohol, and not in any respect like acids, aldehydes, ketones, etc. Between it and ordinary alcohol there is, however, one marked difference. The reactions characteristic of ordinary alcohol can be carried

further with this substance. Thus, while from the former only one metallic derivative, C_2H_5OK, can be obtained with any one metal, from ethylene alcohol two such derivatives can be obtained, viz., $C_2H_5O_2K$ and $C_2H_4O_2K_2$. One hydrogen and all the oxygen of ordinary alcohol are replaced by chlorine under the influence of the chlorides of phosphorus, the product C_2H_5Cl being formed; while, according to the relative quantity of the chloride of phosphorus brought into action, two different chlorides can be obtained from ethylene alcohol, viz., C_2H_5OCl and $C_2H_4Cl_2$. By oxidation ordinary alcohol yields but one acid, and that is monobasic. By oxidation of ethylene alcohol two different acids can be obtained. One of these, of the formula $C_2H_4O_3$, is monobasic, and has the peculiarity that it combines in itself the properties of an acid and an alcohol; the other, of the formula $C_2H_2O_4$, is dibasic.

These facts can be best explained by assuming that in ethylene alcohol there are two hydroxyls, or, in other words, that the characteristic grouping of the hydrogen and oxygen in ordinary alcohol is twice repeated in ethylene alcohol.

This conception of the nature of ethylene alcohol finds expression in the formula $C_2H_4\begin{cases}OH\\OH\end{cases}$.

This formula has been verified by a synthesis, the principle of which is shown by the equation:—

$$C_2H_4Br_2 + 2Ag(OH) = C_2H_4\begin{cases}OH\\OH\end{cases} + 2AgBr.$$

Accepting the formula, the reactions referred to can be interpreted thus:—

$$C_2H_4\begin{cases}OH\\OH\end{cases} + K = C_2H_4\begin{cases}OK\\OH\end{cases} + H;$$

$$C_2H_4\begin{cases}OK\\OH\end{cases} + K = C_2H_4\begin{cases}OK\\OK\end{cases} + H;$$

$$C_2H_4\begin{cases}OH\\OH\end{cases} \text{ gives } C_2H_4\begin{cases}Cl\\OH\end{cases} \text{ and } C_2H_4\begin{cases}Cl\\Cl\end{cases};$$

$$C_2H_4\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix} \quad \text{gives} \quad \begin{matrix}COOH\\ |\\ CH_2OH\end{matrix} \quad \text{and} \quad \begin{matrix}COOH\\ |\\ COOH\end{matrix}.$$

Hydroxy-acetic or glycolic acid. Oxalic acid.

Considering the oxidation products, and recalling what has already been said concerning the transformation of alcohols into acids, we are led to the belief that in ethylene alcohol there are two primary alcohol groups, CH_2OH, and that each of these in turn can be converted into carboxyl. In the light of these considerations, the formula $\begin{matrix}CH_2OH\\ |\\ CH_2OH\end{matrix}$ for ethylene alcohol becomes extremely probable.

Monohydroxy-monobasic Acids, $C_nH_{2n}O_3$.—The simple fatty acids have the general formula $C_nH_{2n}O_2$. There is a series of monobasic acids, clearly related to these, which have the formula $C_nH_{2n}O_3$. The simplest of these is identical with the first product of oxidation of ethylene alcohol. It is known as *glycolic* or *hydroxyacetic acid*, and has the formula $C_2H_4O_3$. It has the properties of an alcohol as well as an acid. The formula $\begin{matrix}CH_2OH\\ |\\ COOH\end{matrix}$ is in accordance with the facts. The presence of the alcoholic hydroxyl is shown in the same way as in the case of simple alcohols. The formula suggests the possibility of converting the compound into a dibasic acid of the formula $\begin{matrix}COOH\\ |\\ COOH\end{matrix}$, a transformation which, as we have seen, can actually be effected.

The synthesis of the acid furnishes further proof of the correctness of the view expressed by the formula. It has been prepared by treating chlor- or bromacetic acid with silver hydroxide:—

$$\begin{matrix}CH_2Br\\ |\\ COOH\end{matrix} + AgOH = \begin{matrix}CH_2OH\\ |\\ COOH\end{matrix} + AgBr.$$

Bromacetic acid. **Glycolic acid.**

All acids which, like glycolic acid, can be regarded as

simple acids in which hydroxyl takes the place of hydrogen, are known as *hydroxy-acids.*

Hydroxypropionic Acids, $C_2H_4\left\langle\begin{array}{l}OH\\COOH\end{array}\right.$.—These acids are monohydroxyl derivatives of propionic acid. It has been pointed out that of the mono-substitution-products of propionic acid there are two varieties, known as the α- and β-compounds. Accordingly, we should expect the existence of two hydroxy-propionic acids of the formulas:—

$$\begin{array}{ccccc} & H & & OH & \\ & | & & | & \\ H— & C & — & C & —CO.OH \\ & | & & | & \\ & H & & H & \end{array} \quad \text{and} \quad \begin{array}{ccccc} & H & & H & \\ & | & & | & \\ HO— & C & — & C & —CO.OH. \\ & | & & | & \\ & H & & H & \end{array}$$

These are the only ones the existence of which is foretold by the theory. Nevertheless, no less than four compounds have been described as hydroxy-propionic acids. These are:—

1. α-*Hydroxy-propionic acid*, or inactive ethylidenelactic acid. This is ordinary lactic acid, obtained by fermentation of milk.

2. *Paralactic acid*, or sarcolactic acid, also called ethylidenelactic acid.

3. *Lævo-lactic acid.*

4. *Hydracrylic acid.*

α-Hydroxy-propionic acid is obtained by substituting hydroxyl for chlorine in α-chlorpropionic acid. It is also made from the compound $CH_3.CH\left\langle\begin{array}{l}Cl\\Cl\end{array}\right.$ (obtained from aldehyde by treatment with phosphorus pentachloride) by substituting hydroxyl for one and carboxyl for the other chlorine atom. It is optically inactive, that is, has no perceptible effect on polarized light.

Paralactic acid acts towards reagents like ordinary lactic acid, and is hence shown to belong to the α-series. Unlike the ordinary acid, however, it exerts a decided influence on polarized light. Lævo-lactic acid also conducts itself like an α-acid, but it turns the plane of polarization to the left, while paralactic acid turns the plane to the right.

The isomerism of these three acids cannot be explained

by our ordinary formulas. A suggestion made by LeBel, and by van't Hoff furnishes an entirely satisfactory explanation. This suggestion has reference to a possible new kind of isomerism in the case of optically active substances. It will be briefly treated in the last section. Attention may, however, here be directed to the fact that ethylidene-lactic acid contains what has been called (see p. 207) an *asymmetrical carbon atom*,

$$\begin{array}{ccccc} & & OH & & \\ & & | & & \\ H_3C & — & C & — & COOH \\ & & | & & \\ & & H & & \end{array}$$

It is upon this fact that the explanation of this peculiar kind of isomerism is based.

Hydracrylic acid is made from β-iodo-propionic acid, and is hence a β-compound. It is also made from ethylene by adding hypochlorous acid and substituting carboxyl for the chlorine in the resulting compound, as has been explained (see p. 212).

Lactones.—The γ- and δ-hydroxy acids are extremely unstable. When set free from their salts they lose the elements of water and are thus transformed into neutral compounds called lactones. As these have neither alcoholic nor acid properties, it is believed that they should be represented by such formulas as the following:—

$$\begin{array}{ccc} 1. & 2. & 3. \\ \begin{array}{l} CH_2.CH_2.CH_2, \\ \;|\qquad\qquad\;\; | \\ O\text{———}CO \end{array} & \begin{array}{l} CH_2.CH_2.CH_2.CH_2, \\ \;|\qquad\qquad\qquad\quad | \\ O\text{—————}CO \end{array} & \begin{array}{l} CH_3.CH_2.CH_2.CH_2 \\ \qquad\quad | \qquad\quad\; | \\ \qquad\;\, O\text{———}CO \end{array} \end{array}$$

Formulas 1 and 3 represent γ-lactones, and formula 2 a δ-lactone.

The relation between a lactone and the corresponding hydroxy acid is shown as follows:—

$$\begin{array}{l} CH_2.CH_2.CH_2 \\ \;|\qquad\qquad\; | \\ OH\qquad COOH \end{array} = \begin{array}{l} CH_2.CH_2.CH_2 \\ \;|\qquad\qquad\; | \\ O\text{———}CO \end{array} + H_2O.$$

γ-Hydroxy-butyric acid. Butyro-lactone.

Dibasic Acids, $C_nH_{2n-2}O_4$.—*Oxalic acid*, $C_2H_2O_4$, or $\begin{array}{l} COOH \\ | \\ COOH \end{array}$, is the simplest representative of these acids.

It is dibasic, and the *same reactions* by which we are led to conclude that carboxyl, COOH, is present in the monobasic acid lead also to the conclusion that, in the dibasic acids, there are two carboxyls present.

The second member of this series is *malonic acid*, $CH_2\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}$. Of each of these acids only one variety is possible.

The third member is *succinic acid*, $C_2H_4\begin{array}{l}\diagup COOH\\ \diagdown COOH\end{array}$.

Of this there should be two varieties corresponding to the two lactic acids, *or the two series of mono-substitution-products* of propionic acid. For succinic acid may plainly be considered as propionic acid in which a hydrogen atom has been replaced by a carboxyl group. The two succinic acids should have the following formulas:—

$$1.\ \begin{array}{ccccc} & H & & CO.OH & \\ & | & & | & \\ H— & C & — & C & —CO.OH \\ & | & & | & \\ & H & & H & \end{array} \quad \text{and} \quad 2.\ \begin{array}{ccccc} & H & & H & \\ & | & & | & \\ CO.OH— & C & — & C & —CO.OH \\ & | & & | & \\ & H & & H & \end{array}$$

The second formula is that of ordinary *succinic acid*, and the first that of *isosuccinic acid*.

Experimental Evidence.—Ordinary succinic acid is obtained from β-cyanpropionic acid, the constitution of which is known to be $\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ CN— & C & — & C & —CO.OH \\ & | & & | & \\ & H & & H & \end{array}$; and from ethylene cyanide, $\begin{array}{l} CH_2.CN \\ | \\ CH_2.CN \end{array}$, which is obtained by treating ethylene bromide with potassium cyanide.

Isosuccinic acid is obtained from α-cyanpropionic acid, which is $\begin{array}{ccccc} & H & & CN & \\ & | & & | & \\ H— & C & — & C & —COOH \\ & | & & | & \\ & H & & H & \end{array}$.

Triacid Alcohols and Tribasic Acids.

Glycerin.—Only one alcohol is well known which contains three hydroxyl groups. This is glycerin. Such alcohols are known as triacid alcohols. The formula of glycerin is

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

. This formula is very probable, because, as a result of a large number of observations on carbon compounds, it seems to be a law that one carbon atom cannot, except under peculiar conditions, hold in combination more than one hydroxyl group. If this be true, the above formula is the only one possible for glycerin. But, again, by oxidation, glycerin yields a monobasic acid containing the same number of carbon atoms; and, by further oxidation, a dibasic acid also containing the same number of carbon atoms. These facts show that the group CH_2OH occurs twice in glycerin. But if there are two groups CH_2OH present in glycerin, then the formula above accepted must be correct.

Glyceric Acid is obtained by partially oxidizing glycerin. As the acid contains the same number of carbon atoms as glycerin contains, it is assumed that the oxidation consists in a transformation of the primary alcohol group CH_2OH into $COOH$; hence, the formula of glyceric acid is

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

. According to this, a dibasic acid,

$$\begin{array}{l} COOH \\ | \\ CHOH \\ | \\ COOH \end{array}$$

, ought to be obtained by oxidizing glyceric acid, just as this dibasic acid is obtained by oxidizing glycerin. This transformation has been effected.

More Complex Alcohols and Acids.

Among the best known substances of greater complexity analogous to those thus far considered are *tartaric acid* and *citric acid*. The former is a dibasic acid containing, in addition to the two carboxyl groups, two alcoholic hydroxyl groups. It is hence a dibasic tetratomic acid. It is dioxysuccinic acid, and must have the formula $\begin{matrix} CH.OH.COOH \\ | \\ CH.OH.COOH \end{matrix}$. It is obtained from dibromsuccinic acid by treating the latter with water, thus—

$$\underset{\text{Dibromsuccinic acid.}}{\begin{matrix} CHBr.COOH \\ | \\ CHBr.COOH \end{matrix}} + 2H_2O = \underset{\text{Tartaric acid.}}{\begin{matrix} CH.OH.COOH \\ | \\ CH.OH.COOH \end{matrix}} + 2HBr.$$

As in the case of the hydroxy-propionic acids, there are substances isomeric with tartaric acid, for which the commonly accepted theories of constitution do not account. It is highly probable that we have here to deal with conditions of structure similar to those met with in connection with the hydroxy-propionic acids. Tartaric acid, like α-hydroxy-propionic acid, contains an *asymmetrical carbon atom*, $\begin{matrix} & OH & \\ & | & \\ H— & C & —COOH \\ & | & \\ & CH & \end{matrix}$, or, rather, it contains two such atoms.

Citric acid is tribasic, containing, in addition to its three carboxyl groups, one alcoholic hydroxyl. These facts are represented in the formula $C_3H_4(OH)\left\{\begin{matrix} COOH \\ COOH \\ COOH \end{matrix}\right.$.

In addition to the compounds treated, there are others still more complex, and derived from the marsh-gas hydrocarbons by the substitution of five and six alcoholic hydroxyls, etc., for hydrogen. Of those containing five hydroxyls, there is only one representative known. Of

those containing six substituting groups, however, a large number are known. Among these are the different varieties of sugars, cellulose, and starch; and the acids which are derived from them. Of late, much progress has been made in the study particularly of those sugars that belong to the same class as grape-sugar or glucose. Many new sugars have been prepared and the relations between them established by the aid of the conceptions of stereo-chemistry as advanced by van't Hoff.

An examination of the alcohols referred to in the preceding pages reveals the fact that the simplest mon-acid alcohol, CH_4O, contains only one carbon atom; the simplest di-acid alcohol, $C_2H_6O_2$, contains two; the simplest tri-acid alcohol, $C_3H_8O_3$, contains three; the simplest tetracid alcohol, $C_4H_{10}O_4$, contains four; and the simplest hex-acid alcohol contains six. This is another illustration of the truth that, except under peculiar conditions, one carbon atom can hold in combination but one hydroxyl.

Cyanogen Compounds.

In speaking of the group CN, under the head of substitution, it was shown that in the cyanides, the arrangement is probably R—C—N (see p. 164). Cyanogen itself is commonly represented by the formula

$$\begin{array}{l} C\text{—}N \\ | \\ C\text{—}N \end{array} \quad \text{or} \quad \begin{array}{l} C\equiv N \\ | \\ C\equiv N \end{array}.$$

The simplest compound of cyanogen is hydrocyanic acid, which probably consists of the group —C—N united with hydrogen, viz., H—C—N or H—C$\equiv$N, though some facts indicate that there is an isomeric acid of the formula C—N—H or C$\equiv$N—H.

The hydrogen atom of this acid can be replaced by a variety of groups or other elements, as, for instance, OH, SH, NH_2, etc. Thus, a large number of derivatives are obtained which have a constitution similar to that of the acid. Thus we have *cyanic acid*, HO—C—N; *sulphocyanic acid*, HS—C—N; *cyanamide*, H_2N—C—N, etc.

It has already been shown that there are compounds containing the group C—N— (or C$\equiv$N—) called isocy-

anides, which are isomeric with the hydrocarbon cyanides, and evidence for the formula C—N— has also been given (see *ante*, p. 165).

Mustard Oils. — Sulphocyanic acid, HS—C—N or HS—C≡N, like other acids, yields salts and ethereal salts by exchanging its hydrogen for metals or hydrocarbon residues. Examples are potassium sulphocyanate, KS—C—N; methyl sulphocyanate, CH_3—S—C—N, etc. Running parallel to the salts of sulphocyanic acid is a series of compounds known as mustard oils. These have the same composition, but entirely different properties and constitution.

The simplest representative of this series is *methyl mustard oil*, which has the constitution expressed by the formula S—C—N—CH_3 or S=C=N—CH_3. A number of corresponding compounds are known, one of which is *allyl mustard oil*, S—C—N—C_3H_5. This is the oil obtained from black mustard seed.

The evidence in favor of the constitution assigned to the mustard oils is as follows:—

Ethyl mustard oil is formed by the action of thiocarbonyl chloride on ethylamine, thus:—

$$CSCl_2 + NH_2{-}C_2H_5 = SC{=}N{-}C_2H_5 + 2HCl.$$

It is also formed by a somewhat circuitous method. When carbon disulphide, CS_2, is brought in contact with ethylamine, $N\left\langle\begin{matrix}C_2H_5\\H\\H\end{matrix}\right.$, the ethylamine salt of ethylsulphocarbamic acid is formed, thus:—

$$CS_2 + 2(NH_2.C_2H_5) = CS\left\langle\begin{matrix}NH.C_2H_5\\SH.NH_2.C_2H_5\end{matrix}\right. .$$

By appropriate reactions this salt is resolved into ethylamine, hydrogen sulphide, and ethyl mustard oil. The decomposition can be best interpreted as follows:—

$$CS\left\langle\begin{matrix}N\boxed{H}.C_2H_5\\\boxed{SH}.\underline{NH_2.C_2H_5}\end{matrix}\right.$$

Hence the resulting mustard oil apparently retains an atom of sulphur united with carbon alone, and the carbon in turn is probably also united directly with the residue of ethylamine, $—N.C_2H_5$. A study of the decomposition of ethyl mustard oil also leads to the formula above given. With water or hydrochloric acid it yields ethylamine, carbon dioxide, and hydrogen sulphide; with nascent hydrogen it yields ethylamine, formic thioaldehyde, and hydrogen sulphide. The production of ethylamine indicates clearly that in the mustard oil the ethyl group is in combination with the nitrogen atom; and the production of formic thioaldehyde, which differs from formic aldehyde, H.COH, only in containing sulphur in the place of oxygen, also indicates that in ethyl mustard oil the sulphur atom is in combination with carbon. These results are embodied in the formula accepted for the mustard oil.

The ethereal salt of sulphocyanic acid, which is isomeric with ethyl mustard oil, conducts itself towards reagents in an entirely different manner. It never yields ethylamine, but always a compound in which the ethyl group is in combination with sulphur, as ethyl sulphide or ethyl-sulphonic acid; while the nitrogen is split off in combination with hydrogen alone, or with carbon, hydrogen, and oxygen.

Derivatives of Carbonic Acid.

The salts of carbonic acid have the general formula M_2CO_3. They are derived from a dibasic acid, H_2CO_3. This acid being dibasic probably contains two hydroxyl groups, and hence we are led to the formula $CO\begin{cases}OH\\OH\end{cases}$ for carbonic acid. This acid is not known except in solution in water. If the attempt is made to prepare it from its salts, the compound CO_2 is always obtained. It has already been stated that it appears to be a law that one carbon atom cannot hold in combination more than one hydroxyl group. This breaking down of carbonic acid into water and the oxide is an indication of the truth of the law. The acid appears to be formed when the oxide is conducted into water.

Though carbonic acid itself is practically unknown, a large number of its derivatives are well known. These are obtained, 1, by replacing the hydrogen of the acid by elements or groups; 2, by replacing one or both of the hydroxyl groups in the same way; 3, by replacing the oxygen by sulphur. Thus we obtain first salts and ethereal salts; then compounds, such as *carbonyl chloride*, $\mathrm{C}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\\ \mathrm{Cl}\end{matrix}\right.$, *carbon sulphoxide*, $\mathrm{C}\left\langle\begin{matrix}\mathrm{S}\\ \mathrm{O}\end{matrix}\right.$, carbon disulphide, $\mathrm{C}\left\langle\begin{matrix}\mathrm{S}\\ \mathrm{S}\end{matrix}\right.$; and finally such compounds as *sulphocarbonic acid*, $\mathrm{CS}\left\langle\begin{matrix}\mathrm{SH}\\ \mathrm{SH}\end{matrix}\right.$, *xanthogenic acid*, $\mathrm{CS}\left\langle\begin{matrix}\mathrm{O.C_2H_5}\\ \mathrm{SH}\end{matrix}\right.$, etc.

Among the most important derivatives of carbonic acid is the amide, *urea* or *carbamide*, which has the constitution expressed by the formula $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right.$.

The evidence in favor of this formula is as follows:—

It is formed by the action of carbonyl chloride on ammonia, thus:—

$$\mathrm{COCl_2} + 2\mathrm{NH_3} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + 2\mathrm{HCl};$$

also by the action of ammonia upon ethyl carbonate, thus:—

$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{OC_2H_5}\\ \mathrm{OC_2H_5}\end{matrix}\right. + 2\mathrm{NH_3} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + 2(\mathrm{C_2H_6O}).$$

The latter is a general reaction used for the preparation of acid amides from the ethereal salts.

Urea has the power of uniting with bases, acids, and salts, and forming with them crystallized compounds. Instead of the ammonia residue $\mathrm{NH_2}$ it may contain residues of the amine bases, as $\mathrm{NH.CH_3}$, $\mathrm{NH.C_2H_5}$, etc. Or, again, one or more of the hydrogen atoms of urea may be replaced by acid residues, such as $\mathrm{C_2H_3O}$, $\mathrm{C_7H_5O}$, etc.

A large number of compounds are allied to and derived from *uric acid*. They have frequently been the subjects of exhaustive investigations, and recently a formula has been proposed for the acid which is in perfect accordance with all the facts learned. It is a weak dibasic acid, but it does not contain two carboxyl groups, for its formula is $C_5N_4H_4O_3$, while a compound which contains two carboxyl groups must of course contain four atoms of oxygen. It has been shown to contain two urea residues differently combined, each of which retains two imide groups, NH. Two syntheses of the acid have recently been effected, and it may now fairly be claimed that its constitution has been determined.

CHAPTER XV.

UNSATURATED COMPOUNDS ALLIED TO THE MARSH-GAS DERIVATIVES.

THE hydrocarbons and their derivatives which have thus far been treated have the peculiarity in common that nothing can be added directly to them. In order to change them something must first be removed from them. When treated with *strong reagents*, the *first kind of action* that takes place is substitution. Thus, marsh-gas, CH_4, and chlorine yield CH_3Cl, CH_2Cl_2, etc., and not CH_4Cl, CH_4Cl_2. Compounds that act in this way are called *saturated compounds*. The condition of saturation is undoubtedly dependent upon the valency of the elements, and, in the terms of the valency hypothesis, it is explained by saying that in the saturated compounds all the bonds or affinities of the elements are satisfied.

There are many compounds that do not act in the manner described. When treated with strong reagents, such as chlorine, bromine, etc., they take these elements up directly. In many cases substitution does not take place until a definite quantity of the element has been added. Addition is the first kind of action. Thus, ammonia and all the substituted ammonias take up acids and other compounds and form addition-products :—

$$NH_3 + HCl = NH_4Cl.$$
$$NH_2.CH_3 + HBr = NH_3.CH_3.Br.$$
$$NH_2CH_3 + CH_3Br = NH_2(CH_3)_2Br.$$

The cyanides are unsaturated, as is shown by their power to take up hydrogen directly :—

$$HCN + 4H = NH_2.CH_3.$$
$$CH_3.CN + 4H = NH_2.C_2H_5.$$

Aldehydes and ketones are also unsaturated, as is shown by their power to take up hydrogen:—

$$CH_3.COH + 2H = CH_3.CH_2OH$$

$$CH_3.CO.CH_3 + 2H = CH_3.CH(OH).CH_3.$$

Further, there are many hydrocarbons which are unsaturated, taking up chlorine, bromine, iodine, hydrochloric acid, hydrogen, etc., and forming addition-products. The simplest example of this kind is ethylene, which has the composition C_2H_4. When this is treated with bromine this reaction takes place:—

$$C_2H_4 + 2Br = C_2H_4Br_2.$$

With hydrobromic acid this reaction takes place:—

$$C_2H_4 + HBr = C_2H_5Br;$$

and with hydrogen this:—

$$C_2H_4 + 2H = C_2H_6.$$

If bromine is allowed to act further upon the compound $C_2H_4Br_2$, no more bromine is added, but hydrogen displaced, and the first result is a reaction of this kind:—

$$C_2H_4Br_2 + 2Br = C_2H_3Br_3 + HBr.$$

What is the difference between saturated and unsaturated compounds? This question has already been discussed in a general way (see *ante*, pp. 99 and 101). The commonly accepted explanation of most unsaturated compounds is that in them certain elements are combined by more than one affinity, while in the saturated compounds only single affinities exist; or, in other words, double or triple linkage of atoms is believed to exist in most unsaturated compounds, while only the condition of single linkage is found in saturated compounds. This explanation is not, of course, applicable to the case of ammonia and its derivatives, though the phenomenon of addition in this case appears to be of the same character as the phenomenon of addition in the other cases referred to. In the cyanides it is assumed that between nitrogen and carbon there is triple linkage, as indicated in the formula $CH_3—C\equiv N$. When hydrogen is taken up this triple linkage is changed to single linkage as represented thus:—

$$CH_3—C\equiv N + 4H = H_3C—H_2C—NH_2,$$

and the carbon and nitrogen, which were triply linked, each takes up two atoms of hydrogen.

In the aldehydes and ketones it is assumed that the oxygen is united to carbon by double linkage, as represented in the formulas,

$$\begin{array}{c}H\\|\\CH_3—C{=}O\end{array}, \quad \begin{array}{c}CH_3—C—CH_3\\\|\\O\end{array},$$

etc. When saturation takes place, the double linkage is broken and single linkage takes its place, as represented in the following equations:—

$$\begin{array}{c}H\\|\\CH_3—C{=}O\end{array} + 2H = \begin{array}{c}H\\|\\CH_3—C—O—H\\|\\H\end{array},$$

$$\begin{array}{c}CH_3—C—CH_3\\\|\\O\end{array} + 2H = \begin{array}{c}CH_3—CH—CH_3\\|\\OH\end{array}.$$

In these cases the carbon and oxygen, which are united by double linkage, each takes up one atom of hydrogen.

A similar explanation is sometimes offered for the saturation of ferrous chloride and similar compounds. The view is expressed in this equation:—

$$\begin{array}{c}Cl\quad Cl\\|\quad\;\;|\\Fe{=}Fe\\|\quad\;\;|\\Cl\quad Cl\end{array} + 2Cl = \begin{array}{c}Cl\quad Cl\\|\quad\;\;|\\Cl—Fe—Fe—Cl.\\|\quad\;\;|\\Cl\quad Cl\end{array}$$

Now, turning to ethylene, the unsaturated condition of this compound can be explained in the same way, and the addition of hydrogen, bromine, etc., to it appears to be a phenomenon of the same kind as those just considered. The reactions with hydrogen, hydrobromic acid, and bromine are represented thus:—

$$\begin{array}{c}CH_2\\\|\\CH_2\end{array} + \begin{array}{c}H\\|\\H\end{array} = \begin{array}{c}CH_3\\|\\CH_3\end{array}$$

$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} H \\ | \\ Br \end{array} = \begin{array}{l} CH_3 \\ | \\ CH_2Br \end{array}$$

$$\begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{c} Br \\ | \\ Br \end{array} = \begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}.$$

There is independent evidence that when bromine is added to ethylene one atom of bromine combines with each carbon atom and not both with one; therefore it appears probable that in the other additions the action takes place in the same way.

It is clear that a satisfactory explanation of what is meant by double linkage cannot be given until it is known what single linkage is. The condition of double linkage is generally admitted in such compounds as the oxides of polyvalent elements, as $Ca{=}O$, $Ba{=}O$, $Cu{=}O$, $C{=}O$, $C\begin{array}{l} {/\!\!/}O \\ {\backslash\!\!\backslash}O \end{array}$, etc., and many familiar reactions are explained in the same way as the cases above discussed. Thus, for example, the action of water on calcium oxide is a reaction of the same kind as that which takes place when hydrobromic acid, etc., act upon ethylene:

$$\begin{array}{c} Ca \\ \| \\ O \end{array} + \begin{array}{c} O{-}H \\ | \\ H \end{array} = \begin{array}{l} Ca{-}O{-}H \\ | \\ O{-}H \end{array}.$$

According to this, calcium oxide is an unsaturated compound in the same sense in which ethylene is unsaturated. While, then, we cannot say that the condition of double or triple linkage does, as a matter of fact, exist in unsaturated compounds, still the hypothesis is convenient and helpful, and may be held tentatively in dealing with the phenomena of unsaturation.

The chief arguments in favor of the view as applied to carbon compounds are the following:—

1. Among carbon compounds the condition of unsaturation does not generally occur except in cases in which there is the possibility of double or triple linkage between carbon atoms. There is, for example, no compound CH_2 and none of the composition CCl_2 or CBr_2

On the other hand, there is the compound CO, which

cannot be explained by the hypothesis under discussion. It cannot be assumed that in this compound the oxygen is quadrivalent without doing violence to nearly all facts known to us in regard to oxygen. Nor can we assume that carbon is bivalent towards oxygen, for it has the power of taking up additional oxygen and thus becoming saturated. It is unsaturated, but apparently in a different way from ethylene. The existence of two oxides of carbon and only one hydrogen compound with one carbon atom in the molecule is a fact of the same kind as that noticed in connection with sulphur, phosphorus, nitrogen, chlorine, and many other elements, each of which forms but one compound with hydrogen, but more than one with oxygen.

2. The second argument in favor of the double and triple linkage hypothesis is that, when the unsaturated compound becomes saturated, an equal number of atoms or groups is added to each of the atoms between which the complex linkage is assumed. This indicates that there is some condition between these atoms that affects both in the same way.

It is held by some that, in using the signs indicating double and triple linkage, we go further than we are justified in going by what we actually know. This is undoubtedly true. We do not know that anything which can fairly be called double linkage ever occurs in a compound. At the same time, taking all the facts into consideration, the hypothesis seems justified, but the sign must not be interpreted literally. Whether double linkage exists in ethylene or not, this hydrocarbon and a large number of related compounds have a certain property in common which may conveniently be expressed by the same sign in them all.

The common property is their power to take up two atoms of hydrogen, bromine, etc., or a molecule of hydrochloric, hydrobromic acid, etc. The double line = between carbon atoms may then be used as a sign of the ethylene condition, whatever that may be, and it indicates the power on the part of the compound represented to take up two additional univalent atoms.*

* For an instructive discussion of this subject see particularly Lossen, Annalen der Chemie, vol. 204, p. 265.

Ethylene and Derivatives.—In connection with ethane derivatives it was stated that two chlorides are known, both of which have the formula $C_2H_4Cl_2$. One of these is obtained from aldehyde by replacing the oxygen atom by two chlorine atoms; hence its formula was assumed to be $CHCl_2.CH_3$. The isomeric compound has the formula

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

The latter is obtained from ethylene by direct addition of chlorine. Hence it is concluded that ethylene itself is symmetrical, *i. e.*, that each carbon atom in it holds in combination two hydrogen atoms, giving the constitution expressed by the formula $H_2C=CH_2$.

Propylene, etc.—The remaining hydrocarbons of this series are obtained for the most part by treating the chlorides, bromides, or iodides of the hydrocarbons of the methane series with alcoholic potassa, by which means the molecule ClH, BrH, or IH is abstracted from the compound. Thus, from C_3H_7I is obtained C_3H_6; from C_4H_9I is obtained C_4H_8, etc.

In many cases the method of formation of the hydrocarbon shows at once what its constitution is. In some cases a doubt exists even after all the methods of formation and the products of decomposition are taken into consideration.

Alcohols.—Theoretically a series of alcohols is possible, derived from the hydrocarbons of the ethylene series by the replacement of one hydrogen atom by one hydroxyl group. Only one such alcohol is well known. This is allyl alcohol, $C_3H_5.OH$, or $CH_2=CH.CH_2.OH$.

Evidence.—Allyl alcohol differs from propyl alcohol in containing two hydrogen atoms less. Now, by treating allyl alcohol with nascent hydrogen, it is converted into normal propyl alcohol, which, as we have seen, has the constitution

$$\begin{array}{c} \;\;\;H\;\;\;H\;\;\;H \\ \;\;\;|\;\;\;\;|\;\;\;\;| \\ H-C-C-C-OH. \\ \;\;\;|\;\;\;\;|\;\;\;\;| \\ \;\;\;H\;\;\;H\;\;\;H \end{array}$$

Hence it is assumed that in allyl

alcohol, as well as in propyl alcohol, the hydroxyl is in combination with one of the terminal carbon atoms, and, accordingly, it must be either $CH_2{=}CH{-}CH_2.OH$ or $CH_3{-}CH{=}CH.OH$.

Acrylic acid, which is obtained from allyl alcohol by oxidation, is formed from β-iodo-propionic acid by the abstraction of hydriodic acid. β-Iodo-propionic acid, further, is formed from acrylic acid by the addition of hydriodic acid. If the formula for β-iodo-propionic acid $CH_2I{-}CH_2{-}COOH$ is correct, it follows that the formula $CH_2{=}CH{-}COOH$ for acrylic acid is more probable than $CH_3{-}CH{=}COOH$. Indeed, according to the valency hypothesis, the latter formula represents an impossible compound. If the formula $CH_2{=}CH{-}COOH$ for acrylic acid is correct, then the first of the two formulas above given for allyl alcohol is probably correct.

Acids.—Acrylic acid apparently bears the same relation to allyl alcohol that acetic acid bears to ordinary alcohol. Still, ordinary oxidizing agents do not convert the alcohol into the acid. This is probably due to the instability of the unsaturated compound. Chromic acid converts allyl alcohol into the corresponding aldehyde, acrolein, but continued action of the oxidizing agent leads to the formation of formic acid. On the other hand, acrolein is converted into acrylic acid by means of a less active agent than chromic acid, as, for example, silver oxide. Further, if the alcohol be first converted into a saturated compound by the addition of bromine, the resulting dibrompropyl alcohol conducts itself towards oxidizing agents the same as normal propyl alcohol. It yields a dibrompropionic acid, and this, when treated with zinc, loses bromine and yields acrylic acid. The reactions are:—

$$1.\quad \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2OH \end{array} \quad + \quad Br_2 \quad = \quad \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2OH \end{array}\ .$$

$$2.\quad \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ CH_2OH \end{array} \text{ by oxidation yields } \begin{array}{l} CH_2Br \\ | \\ CHBr \\ | \\ COOH \end{array}\ .$$

$$3. \quad \begin{array}{c} CH_2Br \\ | \\ CHBr \\ | \\ COOH \end{array} + Zn = \begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ COOH \end{array} + ZnBr_2.$$

These changes lead to the formula $\begin{array}{c} CH_2 \\ \| \\ CH \\ | \\ COOH \end{array}$ for acrylic acid. This acid is the first of a series, each member of which differs from the corresponding member of the series $C_nH_{2n}O_2$ by containing two hydrogen atoms less.

Acetylene.— By treating symmetrical dibromethane, $\begin{array}{l} CH_2Br \\ | \\ CH_2Br \end{array}$, with an alcoholic solution of potassium hydroxide, hydrobromic acid is abstracted, and acytelene, a hydrocarbon of the formula C_2H_2 is formed:—

$$C_2H_4Br_2 \quad - \quad 2HBr \quad = \quad C_2H_2.$$

This compound is a representative of a class of unsaturated compounds, differing from the ethylene derivatives in composition the same as the latter differ from the marsh-gas derivatives. The acetylene compounds have the power of taking up four atoms of chlorine or bromine or two molecules of hydrochloric or hydrobromic acid. The reactions with acetylene are illustrated by the following examples:—

$$C_2H_2 \quad + \quad 4Br \quad = \quad C_2H_2Br_4;$$
$$C_2H_2 \quad + \quad 2HBr \quad = \quad C_2H_4Br_2.$$

In regard to the condition existing between the carbon atoms in acetylene and its analogues our knowledge is in much the same state as in regard to the condition between the carbon atoms in ethylene. The arguments advanced in support of the double linkage hypothesis for ethylene and its derivatives may be used in modified form in support of the triple linkage hypothesis for acetylene. Whenever saturation of a compound in which triple linkage is believed to occur takes place, two atoms or groups are added to each of the atoms between which the triple link-

age occurs. This is illustrated by the following reactions:—

$$H_2C=CH_2 + 4Br = Br_2H_2C—CH_2Br_2;$$
$$H—C\equiv N + 4H = H_3C—NH_2.$$

Just as the sign for double linkage is intended mainly to call to mind the fact that the compound in which it occurs has certain properties which are found in ethylene, and may, therefore, be called the sign of the ethylene condition; so the sign for triple linkage should be regarded as the sign of the acetylene condition, and when it is found in a formula it indicates, on the part of the compound represented, the power to take up four atoms or groups and thus to become saturated.

Compounds Containing a Smaller Proportion of Hydrogen.—There are several hydrocarbons known which in some respects seem to be analogous to those already considered, but which differ from them in containing a smaller proportion of hydrogen. The principal of these are valylene, C_5H_6, and dipropargyl, C_6H_6. These take up bromine in larger proportion than the hydrocarbons, which contain more hydrogen. Thus, valylene forms $C_5H_6Br_6$, and dipropargyl forms $C_6H_6Br_8$. The products, it will be noticed, belong to the saturated compounds, the former being a substitution product of pentane, C_5H_{12}, and the latter bearing a similar relation to hexane, C_6H_{14}. Not enough is known about these substances to lead to a definite opinion in regard to their structure. It seems probable, however, that they are similar to ethylene and acetylene. Valylene may be represented by the formula $\begin{array}{l} CH_3—\underset{\underset{CH_2}{\|}}{C}—C\equiv CH \end{array}$, and dipropargyl by $CH\equiv C—CH_2—CH_2—C\equiv CH$. The formulas should, however, be regarded as tentative.

CHAPTER XVI.

BENZENE DERIVATIVES. (AROMATIC COMPOUNDS.)

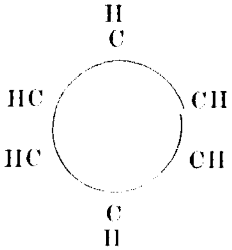
A LARGE class of compounds exists, the members of which possess the property in common that, when decomposed in a number of ways, they yield benzene as one of the products. Benzene itself has the formula C_6H_6. Just as the members of this class of compounds yield benzene as a decomposition product, so, also, they may be built up from benzene by the introduction of a variety of groups or elements in the place of hydrogen. All these compounds bear relations to benzene similar to those which the fatty compounds bear to marsh-gas. In studying the aromatic compounds then, it is of first importance to determine the constitution of benzene itself, as the constitution of the derivatives cannot be understood until that of benzene is known.

Constitution of Benzene.—Whatever view may be entertained regarding the structure of benzene, the following facts must be accounted for:—

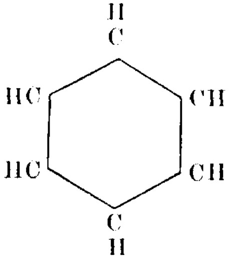
1. Of the substitution products of benzene which contain one substituting group, only one variety is known.
2. Of the substitution products of benzene which contain two substituting groups, three varieties are known, and only three.
3. Of the substitution products of benzene which contain three substituting groups, more than three varieties are known, except in case the substituting groups are all of the same kind, in which case only three varieties are known.
4. Six, and only six atoms of bromine, chlorine, etc., can be added directly to benzene.

A great deal of ingenious experimenting has been gone through with for the purpose of testing the first of these statements. The method adopted may be briefly described. Starting with benzene, C_6H_6, one atom of hydrogen was

replaced by bromine, a product C_6H_5Br, being thus formed. Now a second hydrogen was replaced by some other group, say NO_2, the product $C_6H_4\begin{cases}Br \\ NO_2\end{cases}$ being the result. It is plain that the group NO_2 must occupy a place in the molecule different from that which the bromine occupies. Now the bromine was replaced by hydrogen, leaving the compound $C_6H_5(NO_2)$ with the group NO_2 presumably occupying the same place that it did in the compound $C_6H_4\begin{cases}Br \\ NO_2\end{cases}$. Finally, the group NO_2 was replaced by bromine, and a compound, C_6H_5Br, was obtained in which the bromine replaced a different hydrogen atom from that replaced in the first compound. The two compounds were found to be identical, and the conclusion is drawn that two of the hydrogen atoms bear the same relation to the molecule. In a similar way the examination has been extended to all six of the hydrogen atoms, and the result reached is in accordance with the first general statement. It seems, hence, that all six hydrogen atoms in benzene bear the same relation to the molecule. From this it follows that the molecule of benzene is symmetrically formed. Each one of the hydrogen atoms must be in combination with a single carbon atom, and what is true of one of them must be true of all the others If the attempt is made to represent these ideas by a formula, it is plain that the formula must differ in some way from all those with which we have thus far had to deal. No one of these, representing a molecule with more carbon atoms, is strictly symmetrical. They represent the atoms as arranged in chains open at both ends. The simplest way in which the symmetrical character of benzene can be represented is by means of a circle. We may suppose the six atoms of carbon arranged at equal distances in a circle, and the six hydrogen atoms in combination with them, thus:—

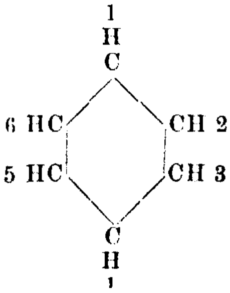


Of course the curved lines have no special significance, and to bring this formula in harmony with other chemical formulas we may write it thus:—



This formula, then, symbolizes the fact that each of the six hydrogen atoms of benzene bears the same relation to the molecule.

Examining the formula with reference to the derivation of di-substitution products, we are led to the conclusion that a compound represented by it ought to yield three classes of di-substitution products. Numbering the hydrogen atoms thus:—

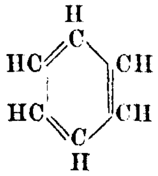


it is plain that there are three kinds of relations which any one hydrogen atom bears to the others considered individually. Thus, the relation of 1 to 2 is different from that of 1 to 3 or 1 to 4. The relation of 1 to 5 is identical with that of 1 to 3, and that of 1 to 6 is identical with that of 1 to 2. Hence, if X be substituted for H.1, and another X for another hydrogen, three different products ought to result according as the second X takes the place of H.2, H.3, or H.4. The same statements hold good, whether we start with H.1 or H.2, or any of the other hydrogen atoms.

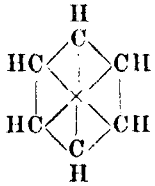
It will thus be seen that the formula is in strict harmony with the observed fact that there are but three classes of di-substitution products of benzene.

In a similar way it can be shown that the formula is in harmony with the fact that of the tri-substitution products containing different substituting groups there are more than three varieties, while of those in which all three substituting groups are the same, there are only three varieties; though not much weight can be attached to this as yet, as the subject has not been investigated to a sufficient extent to furnish a sufficient basis of facts.

There is another fact which, if interpreted by the aid of the valency hypothesis, also speaks in favor of the above formula. This formula does not account for all the bonds of carbon. It is not known what relation exists between these carbon atoms. Various formulas have been suggested with the object of showing how the bonds are disposed of, but they are all open to the serious objection that they try to express relations about which we know practically nothing. At the present stage of our knowledge it makes but little difference whether we write the formula :—

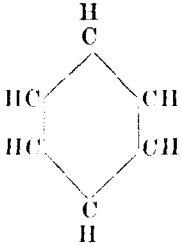


or

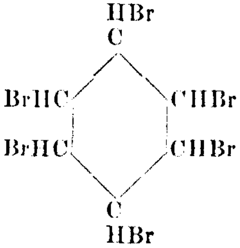


both of which are in use. It is better not to write either, but to use the simple figure above given, which does not

attempt to tell the entire story, but simply to express by a symbol certain ideas to which we are led by a consideration of the facts known to us. Using, then, the simplest formula,



though for the argument it is immaterial which one of the three we use, the idea suggests itself that this hydrocarbon ought to be able to take up bromine; it appears to be unsaturated. If each carbon atom has the power to hold four atoms, then plainly each one ought to be able to take up one atom of bromine. By treatment with bromine, benzene ought to yield an addition-product $C_6H_6Br_6$, or

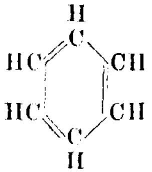


In accordance with this is the fact that, when benzene is treated with bromine in the sunlight, a product, $C_6H_6Br_6$, is actually formed, and not $C_6H_6Br_8$, as in the case of the isomeric hydrocarbon dipropargyl.

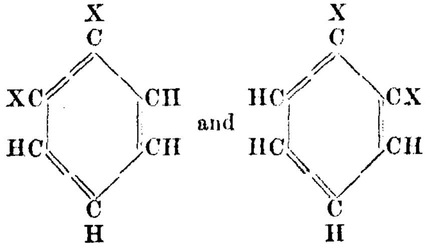
Taking all the facts together then, it is clear that the formula given for benzene represents to the properly trained mind some facts of fundamental importance for the compound. No one claims that this formula, any more than any other in use, represents the actual arrangement of the atoms in space, or that the formula has anything

whatever to do with facts of this order. But it undoubtedly does represent certain truths.

Although our knowledge will not permit us at present to express with any confidence more in regard to the structure of benzene than is expressed by the simple formula, still the question as to the way in which the carbon atoms are united in benzene is one that may legitimately be made the subject of investigation, and it has received a great deal of attention. The formula

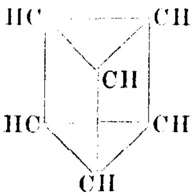


represents the presence of the ethylene condition three times repeated. So far as the formation of addition products is concerned, this formula is satisfactory. On the other hand, it does not represent a perfectly symmetrical compound and the first fact in regard to benzene which must be represented is symmetry. Considering any carbon atom represented in this formula, it is plain that on one side it is united with a carbon atom by single linkage, and, on the other, it is united to a carbon atom by double linkage. Apparently two di-substitution products of the formulas:—

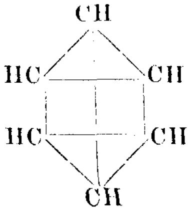


are possible in such a compound. But experiment has shown that the two compounds with the substituting groups in the relations represented in these formulas are identical. In view of the facts several efforts have been made to represent the constitution of benzene by a perfectly symmetrical formula which should at the same time be in accordance with the general notions regarding struc-

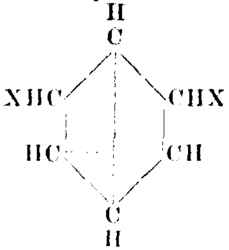
ture. It has been suggested that the constituents of benzene are arranged in the form of a regular prism, thus,

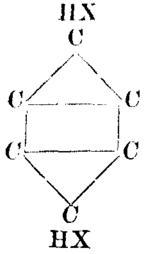


If this be considered simply with reference to the linkage between the carbon atoms, it is identical with this formula,



In the modified prism formula there is no double linkage between carbon atoms. The facts above referred to speak in favor of the prism formula, but they do not decide the question. Recently a chemical method of dealing with the problem has been suggested which may throw light upon it. The considerations upon which the method is based are these: *When a compound in which double linkage occurs becomes saturated, the groups or atoms which are taken up are added to those carbon atoms between which the double linkage occurs.* If, therefore, it were possible to add two atoms or groups to benzene, and it could be shown that they are united with carbon atoms in the

such a fact would be evidence in favor of the view that double linkage had existed between the two adjoining carbon atoms. If the other formula were correct, the position of two groups or atoms in a di-addition product would be represented by this formula 

or this  . As there are methods for de-

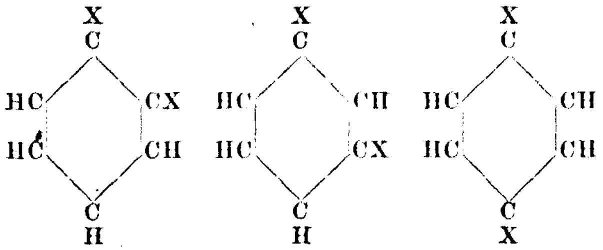
determining the constitution of benzene. One of them is based upon the determination of the heat evolved in the complete combustion of benzene; and another upon observations on the refracting power of benzene. As the former method leads to the conclusion that there are nine single linkages in benzene; and the latter method leads to the conclusion that the formula with three double linkages and three single linkages is correct, it is clear that one of the methods must be defective, and further investigation is necessary.

Substitution Products of Benzene.—Of mono-substitution products there is only one variety. There is only one monochlorbenzene, C_6H_5Cl; only one hydroxybenzene, or phenol, C_6H_5OH; only one benzoic acid, $C_6H_5.COOH$; only one toluene, $C_6H_5.CH_3$, etc., etc. The constitution of most of these derivatives is very simple. There is a peculiarity, however, connected with those which are formed by replacing one hydrogen atom of benzene by a hydrocarbon residue. The simplest compound formed in this way is toluene, which consists of benzene in which a hydrogen atom has been replaced by the methane residue, methyl, CH_3; if, instead of the residue CH_3, ethyl, C_2H_5, is introduced, ethylbenzene, $C_6H_5C_2H_5$, which is plainly a homologue of toluene, is obtained; so, also, the residues C_3H_7, C_4H_9, C_5H_{11}, etc. may be introduced, and thus an homologous series of aromatic hydrocarbons is obtained, all of which are mono-substitution products of benzene. These may, further, all be regarded as substitution products of the hydrocarbons of the methane series. Accordingly, of toluene and ethylbenzene, which are mono-substitution products, of methane and ethane respectively, only one variety is possible; while of the next homologue, or propylbenzene, $C_6H_5.C_3H_7$, two varieties are possible, corresponding to the α- and β-mono-substitution products of propyl, or to the propyl and isopropyl compounds (which see). The principal members of the series of hydrocarbons thus referred to are:—

Benzene,	C_6H_6.
Toluene or methylbenzene,	C_7H_8 or $C_6H_5.CH_3$.
Ethylbenzene,	C_8H_{10} or $C_6H_5.C_2H_5$.
Propylbenzene,	C_9H_{12} or $C_6H_5.C_3H_7$.
Butylbenzene,	$C_{10}H_{14}$ or $C_6H_5.C_4H_9$.
Amylbenzene,	$C_{11}H_{16}$ or $C_6H_5.C_5H_{11}$.

Of these hydrocarbons two classes of mono-substitution products are possible, viz., those in which the substituting group or element is situated in the *benzene ring*, and those in which the substituting group or element is situated in the other residue. These other residues, however they may be constituted, are known as *side chains*. It is plain that substitution-products of the latter kind correspond closely to those of the hydrocarbons of the methane series, and hence they need no special consideration here. If a substituting group or element enters into the benzene ring of any of these hydrocarbons, of course we have no longer to deal with mono-substitution products of benzene.

Di-substitution Products.—The three classes of di-derivatives of benzene, which we have above recognized as possible, have been designated respectively as *ortho, meta,* and *para compounds*, or, by others, as 1.2, 1.3, and 1.4 compounds. The former expressions are to be preferred, for they are independent of any hypothesis concerning the positions of the substituting groups. It is usual to consider the expressions ortho and 1.2, meta and 1.3, para and 1.4, as identical, but this implies that the following formulas have been proved, while they have not been, although they have been rendered extremely probable.



Ortho compound. Meta compound. Para compound.

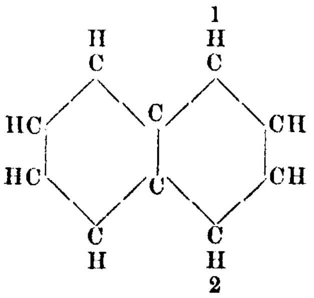
What we really know is that there are three classes of these di-substitution products, and that the members of any one of these classes can be converted into one another, thus showing that they are allied. Any three varieties of a di-substitution product of benzene may be taken as the basis of classification of all the di-substitution products.

Thus, the three isomeric, dicarbonic acids of benzene, $C_6H_4\langle^{COOH}_{COOH}$, viz., phthalic, isophthalic, and terephthalic acids may be taken for this purpose. All di-substitution products that can be converted into phthalic acid are known as ortho compounds, all that can be converted into isophthalic acid are known as meta compounds, and all that can be converted into terephthalic acid are known as para compounds.

The conversion into these acids need not always be direct. If it is possible to convert a compound into another, which, in its turn, can be converted into one of the above acids, the same conclusion is drawn as in the case of a direct conversion. Of course, the accuracy of the conclusions drawn with reference to the constitution of di-substitution products depends upon the trustworthiness of the reactions employed in effecting the conversions. Some reactions employed for this purpose have been found to give inaccurate results, that is to say, the products resulting from an application of these reactions belong to different series from those to which the original compounds belonged. It is probable that some compounds now classified with one series, in consequence of some transformations, may be found by future investigations to belong to a different series.

The formulas given above as representing the relative positions of the substituting groups in ortho-, meta-, and para compounds are based upon the following facts:—

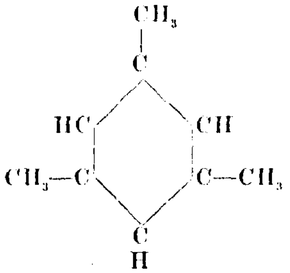
It will be shown that naphthalene (which see) probably has the formula:—



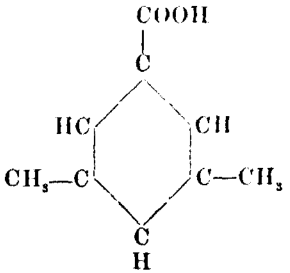
.

By oxidation naphthalene yields phthalic acid It seems probable, therefore, that the carboxyl groups in the acid have the same relative position as that of the groups numbered 1 and 2 in this formula. Consequently, ortho-compounds, or those which can be converted into phthalic acid, are assumed to have their substituting groups in the positions marked 1.2 in the benzene; or, what is the same thing, the substituting groups in ortho-compounds are combined with carbon atoms which are adjacent in the formula.

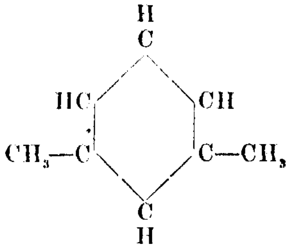
It will also be shown that mesitylene (which see) probably has the formula:—



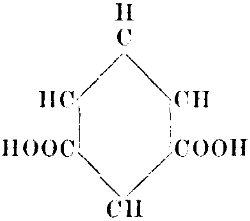
By partially oxidizing this hydrocarbon one methyl is changed to carboxyl, and an acid is obtained of the formula:—



When this acid is heated with lime, carbon dioxide is given off, and a hydrocarbon is obtained of the formula:—



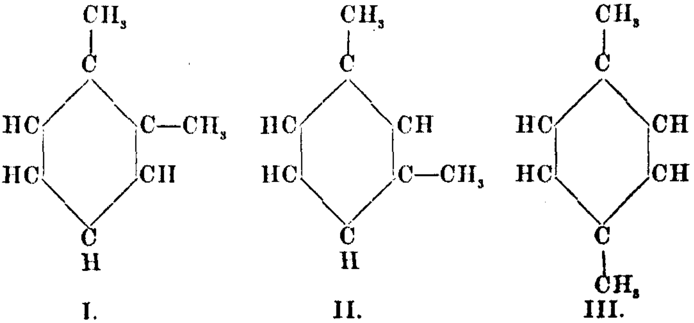
Lastly, when this hydrocarbon is oxidized, both the groups CH_3 are converted into carboxyl, COOH, and the product is isophthalic acid. Hence, if the formula of mesitylene is correct, that of isophthalic acid, which represents it thus,



, is also correct.

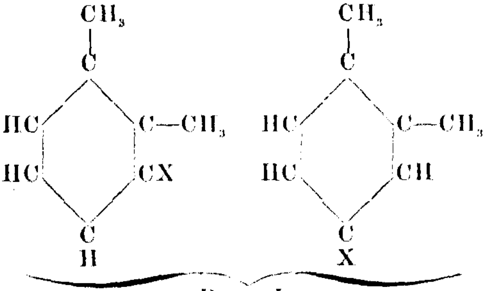
By exclusion, terephthalic acid becomes a 1.4 compound, and, consequently, all para-compounds are 1.4 compounds.

Another method of proof is founded upon the determination of the number of isomeric substitution products that can be obtained from certain di-derivatives of benzene. Take the three xylenes, for example:—

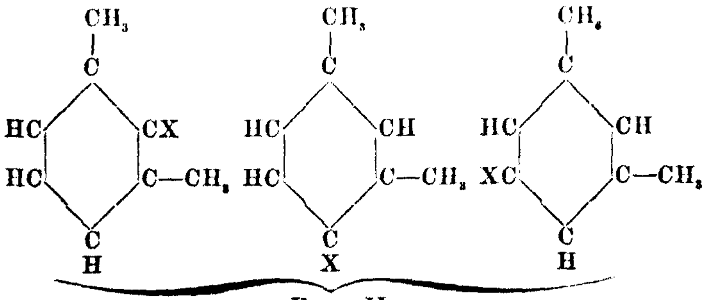


There are three hydrocarbons that are known to be dimethyl derivatives of benzene. The benzene hypothesis furnishes three formulas, but we cannot determine by intuition which one of the formulas to give to one particular hydrocarbon, and yet, if the benzene hypothesis is of value, only one of the three formulas is assignable to any particular hydrocarbon.

An examination of formula III. will show that each of the four hydrogen atoms belonging to the benzene bears exactly the same relation to the molecule. Interpreting this formula in the simplest way, we are led to the conclusion that the compound which it represents ought to yield but one mono-substitution product with any one agent, for it should make no difference which one of the four hydrogen atoms is replaced. This is not true of the other two formulas I. and II. The compound represented by formula I. ought to yield two different mono-substitution products with any one reagent, and the compound represented by formula II. ought to yield three, thus:—



Form. I.



Form. II.

It has been shown that from one of the three xylenes only one variety of mono-substitution products can be obtained, and the conclusion is drawn that to this one, formula III. should be assigned. This is paraxylene, so that we are led by this method of proof to exactly the same conclusion as by the methods already considered. This method has not been fully applied in the case of the two other hydrocarbons, but sufficient is known in connection with other di-substitution products of benzene to show that some of them yield two, and only two, kinds of derivatives by the introduction of one more substituting group, while others yield three. The former are the ortho-, the latter the meta-compounds.

The above will give a fair idea of the basis upon which the expressions 1.2, 1.3, and 1.4 rest. Some of the principal di-substitution products of benzene are given in the following table, which shows also to which series the compounds belong:—

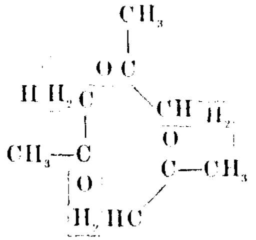
Ortho.	Meta.	Para.
Phthalic acid,	Isophthalic acid,	Terephthalic acid,
Orthoxylene,	Isoxylene,	Paraxylene,
Salicylic acid,	Oxybenzoic acid,	Paroxybenzoic acid,
Pyrocatechin,	Resorcin,	Hydroquinone,
Orthodinitrobenzene,	Metadinitrobenzene,	Paradinitrobenzene,
Orthodibrombenzene,	Metadibrombenzene,	Paradibrombenzene.

Tri-Substitution Products.—One of the most important of the tri-substitution products of benzene is mesitylene. The formula of this hydrocarbon is C_9H_{12}. By oxidation it yields, according to the extent to which the action is allowed to proceed, three different products. The first, mesitylenic acid, $C_8H_9.COOH$, is monobasic; the second, uvitic acid, $C_7H_6.(COOH)_2$, is dibasic; and the third, trimesitic acid, $C_6H_3.(COOH)_3$, is tribasic. All of these acids, when heated with lime, yield either benzene itself or derivatives of benzene. Hence, it is concluded that mesitylene is benzene in which three hydrogen atoms are replaced by three methyl groups, as expressed in the formula $C_6H_3(CH_3)_3$. By oxidation each one of these groups in turn is converted into carboxyl, yielding thus the three acids above mentioned. It still remains, however, to decide what positions these three substituting groups in benzene occupy.

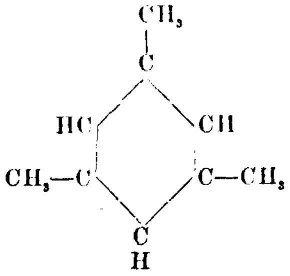
The following considerations lead to the formula for mesitylene given on page 251.

When acetone is treated with concentrated sulphuric acid, water is abstracted, and the residues of three molecules unite to form mesitylene. It seems fair to assume that the three residues have the same constitution, as they are formed under exactly the same conditions, from the same compound. If they are the same, each must be C_3H_4. Three such residues might be formed from acetone, thus:—

Acetone is $CH_3—CO—CH_3$. Three molecules may be arranged:—



If water is abstracted in the manner indicated by the lines, there are left three residues, C_3H_4, and, if these unite, they will form a compound of the constitution represented by the following formula:—



This is the formula accepted for mesitylene; and from this the conclusion is drawn that meta-compounds have their substituting groups in the positions 1.3.

If this formula is examined, it will be seen that each one of the three hydrogen atoms remaining in the ben-

zene occupies a position like that occupied by the other two. Accordingly, if this formula is correct, we should expect to find that, by the introduction of one substituting group into mesitylene, only one product would be formed. This has been found to be true.

Besides mesitylene there are many tri-substitution products of benzene known, containing such elements as Cl, Br, I, and such groups as NO_2, NH_2, SO_2OH, etc. The method by which the position of the substituting groups in these compounds is determined is this: One of the groups is split off, and the constitution of the resulting di-substitution product is determined as above; then, from the original compound some other group is split off, and the constitution of the di-substitution product resulting in this case also determined. It is thus possible to judge of the positions of the three groups with reference to one another. There are not many compounds, however, that can be subjected to this kind of examination with satisfactory results, so that the constitution of the tri-derivatives is not as well known as that of the di-derivatives.

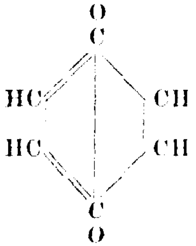
Peculiar Benzene Derivatives.—Among benzene derivatives there are three classes which are not represented, or not as well represented, among the fatty compounds, and hence they require some attention here. These are the *phenols*, *quinones*, and *azo-compounds*.

Phenols.—Phenols are the hydroxyl derivatives of benzene and its homologues, formed by the introduction of hydroxyl in the place of hydrogen in benzene. The corresponding compounds of the hydrocarbons of the methane series are all alcohols, either primary, secondary, or tertiary. The phenols are, however, not alcohols in the sense in which that term has been used up to the present. By oxidation they yield neither aldehydes, acids, nor ketones. If, however, by the expression tertiary alcohol is meant any compound which contains the grouping C(OH), then the phenols are all tertiary alcohols. It is, perhaps, better to restrict the use of the name alcohol to the hydroxyl derivatives of the marsh-gas hydrocarbons.

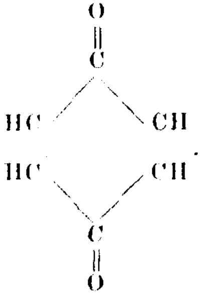
The presence of hydroxyl in phenols can be proved in the same way that it was proved for other compounds containing hydroxyl.

There are monacid phenols, containing only one hydroxyl; diacid phenols, containing two hydroxyls; triacid phenols, containing three hydroxyls, etc.

Quinones.—The quinones are derived from benzene and its homologues by the introduction of two atoms of oxygen in the place of two hydrogen atoms in benzene. Thus, the simplest quinone has the formula $C_6H_4O_2$. Whether the two oxygen atoms form a bivalent group, —O—O—, by combining with each other by means of one of their affinities each, or are in combination with carbon in the carbonyl condition C=O, it has thus far been impossible to decide. The quinones are derived from para-compounds by oxidation, as from hydroquinone, and hence it is concluded that the hydrogen atoms replaced by oxygen in the formation of quinones occupy the para-position with reference to each other. Accordingly, if the para-position is 1.4 the formula of ordinary quinone is either

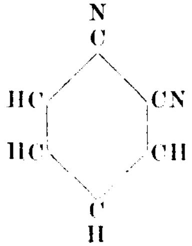


or

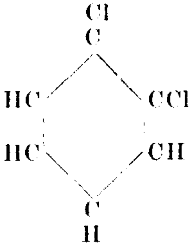


Azo- and Diazo-compounds.—These compounds, as their names imply, are nitrogen derivatives. They are derived from benzene and its homologues by the substitution of nitrogen for hydrogen. We need only consider those which are derived from benzene, as the others are very closely related to them. The diazo-derivatives of benzene are obtained from the salts of aniline or amidobenzene, $C_6H_5.NH_2$, by the action of nitrous acid. Thus, aniline nitrate, $C_6H_5.NH_2.HNO_3$, yields diazobenzene nitrate; aniline sulphate, $(C_6H_5.NH_2).H_2SO_4$, yields diazobenzene sulphate, etc.

If we consider simply the empirical formulas of the salts of diazobenzene thus obtained, we find that they differ from the aniline salts in containing $C_6H_4N_2$ in the place of $C_6H_5NH_2$. The salts consist of the acids plus this group. Thus, the nitrate is $C_6H_4N_2.HNO_3$; the sulphate is $C_6H_4N_2.H_2SO_4$, etc. These formulas do not, however, represent the constitution of the salts. If the group $C_6H_4N_2$ actually existed in these diazo-compounds, it is plain that they would be di-substitution-products, that is to say, two hydrogen atoms of benzene would be replaced by two nitrogen atoms. It was at first supposed that each of these nitrogen atoms played the part of a univalent element, and the diazo-compounds were looked upon as analogous to dichlorbenzene, dinitrobenzene, etc., thus:—



Diazobenzene.



Dichlorbenzene.

It was soon found, however, that, when the diazo-compounds are decomposed, they generally yield derivatives of benzene in which the group C_6H_5 is undoubtedly present. Thus, the following decompositions of diazobenzene sulphate yield, in each case, a derivative containing C_6H_5:—

When boiled with alcohol the products are ethyl-phenyl ether, $C_6H_5O.C_2H_5$, nitrogen and sulphuric acid:—

$$\frac{C_6H_5.N_2.HSO_4}{C_2H_5O \quad H} \text{ yield } \begin{array}{c|c|l} C_6H_5 & N_2 & HSO_4 \\ C_2H_5O & & H \end{array}.$$

When boiled with water the products are phenol, nitrogen, and sulphuric acid:—

$$\frac{C_6H_5.N_2.HSO_4}{OH \quad H} \text{ yield } \begin{array}{c|c|l} C_6H_5 & N_2 & HSO_4 \\ OH & & H \end{array}.$$

When treated with hydriodic acid the products are iodo-benzene, nitrogen, and sulphuric acid:—

$$\frac{C_6H_5.N_2.HSO_4}{I \qquad H} \quad \text{yield} \quad \begin{array}{c|c|c} C_6H_5 & N_2 & HSO_4 \\ I & & H \end{array}.$$

Other reactions indicate as well that the group C_6H_5 is present in the diazo-compounds. But, if this group is present, the two nitrogen atoms must be so combined that they can take the place of one hydrogen atom. Now, if two nitrogen atoms, which have the same valency, be combined, they must either form a neutral group with all its affinities satisfied, or a group which is at least bivalent. Such a bivalent group will be formed, for instance, if two nitrogen atoms are united by means of two affinities each, thus, $—N{=}N—$. If this group should replace one hydrogen atom of benzene, the constitution of the resulting compound would be $C_6H_5—N{=}N—$. Such a compound would be unsaturated. No compound of the formula $C_6H_5N_2$ has been obtained, but all the derivatives of diazobenzene can be explained on the supposition that they are derived from the compound $C_6H_5—N{=}N$.

Accepting the group $C_6H_5—N{=}N—$ as the foundation of the diazo-compounds, these may be formulated as follows:—

$C_6H_5—N{=}N—Br$,	diazobenzene bromide,
$C_6H_5—N{=}N—NO_3$,	diazobenzene nitrate,
$C_6H_5—N{=}N—HSO_4$,	diazobenzene sulphate,
$C_6H_5—N{=}N—OK$,	diazobenzene potassium,
$C_6H_5—N{=}N—NH(C_6H_5)$,	diazobenzene diamidobenzene.

Azobenzene is formed by the reduction of nitrobenzene. Its formula is $C_{12}H_{10}N_2$. As nitrobenzene contains the group C_6H_5 combined with nitrogen, we may assume that azobenzene consists of two such groups $C_6H_5—N{=}$. If these combine in the simplest manner, we should have the formula $\begin{array}{l} C_6H_5—N \\ \qquad \;\; \| \\ C_6H_5—N \end{array}$, expressing the constitution of azobenzene. This is the formula now generally accepted.

According to this, the azo-compounds are very closely related to the diazo-compounds. Both contain the group

—N=N— in combination with C_6H_5. In reality, the azo-compounds differ very much in their chemical conduct from the diazo-compounds. The decompositions which they undergo take place in a manner entirely different from that already noticed as characterizing the decomposition of diazo-compounds.

This difference has led some chemists to abandon the formulas above given for the diazo-compounds, and to propose others in their place. The compounds are supposed to be ammonium compounds of the general formula

$$\begin{array}{l} R—N—R' \\ \quad ⦀ \\ \quad N \end{array}$$

. They contain one quinquivalent and one trivalent nitrogen atom. The relation between aniline nitrate and diazobenzene nitrate is shown thus:—

$$\begin{array}{ll} C_6H_5 & C_6H_5 \\ | & | \\ N—O—NO_2; & N—O—NO_2. \\ ⋮ & ⋮ \\ H_3 & N \\ \text{Aniline nitrate.} & \text{Diazobenzene nitrate.} \end{array}$$

Against the latter view the following facts speak: When diazobenzene nitrate is treated with neutral potassium sulphate, a salt of the formula $C_6H_5—N_2—SO_3K$ is formed according to this equation:—

$$C_6H_5—N_2—NO_3 + SO_3KK = C_6H_5—N_2—SO_3K + NO_3K.$$

When the salt thus obtained is reduced it yields a phenylhdyrazine derivative:—

$$C_6H_5—N_2—SO_3K + H_2 = C_6H_5—N_2H_2—SO_3K;$$

and, finally, when this product is treated with hydrochloric acid, the hydrochloride of phenylhydrazine is formed:—

$$C_6H_5—N_2H_2—SO_3K + HCl = C_6H_5—N_2H_3—HCl + HKSO_4.$$

But the constitution of phenylhydrazine is represented by the formula $C_6H_6—HN—NH_2$. Its formula is easily understood if the constitution of diazobenzene nitrate is $C_6H_5—N=N—NO_3$. In this case the change from the nitrate to phenylhydrazine consists simply in the replacement of the NO_3 group by hydrogen and the saturation

of the compound by hydrogen. In the other case the successive products must be represented in this way:—

$$\begin{array}{llll} C_6H_5-\underset{\underset{\displaystyle N}{|||}}{N}-NO_3, & C_6H_5-\underset{\underset{\displaystyle N}{||}}{N}-SO_3K, & C_6H_5-\underset{\underset{\displaystyle N}{||}}{NH}-SO_3K, & C_6H_5-\underset{\underset{\displaystyle NH}{||}}{NH_2}. \end{array}$$

The formula to which we are thus led for phenylhydrazine is not correct.

Azoxy- and Hydrazo-compounds.—Among other nitrogen compounds which are related to the diazo- and azo-compounds are the *azoxy- and hydrazo-compounds*. These as well as the diazo- and azo-compounds are to be regarded as products of the incomplete reduction of nitro-compounds. When nitrobenzene is treated with nascent hydrogen the final product of the action is aniline, the process being similar to the reduction of nitric acid to hydroxylamine:—

$$N\begin{cases} C_6H_5 \\ O \\ O \end{cases} + 6H = N\begin{cases} C_6H_5 \\ H \\ H \end{cases} + 2H_2O;$$

$$N\begin{cases} OH \\ O \\ O \end{cases} + 6H = N\begin{cases} OH \\ H \\ H \end{cases} + 2H_2O.$$

But just as intermediate products are obtained in the reduction of nitric acid, viz., N_2O_3, NO, N_2O, and N_2, so intermediate products are obtained in the reduction of the nitro-compounds. The relations between the end products and the intermediate products are shown in the following table:—

Nitro-compound, $R.NO_2$.

Azoxy-compound, $\begin{array}{l} R-N \\ \;\;\;\;\;| \\ R-N \end{array}\!\!>O$.

Azo-compound, $R-N=N-R$.
Hydrazo-compound, $R-NH-NH-R$.
Amido-compound, $R-NH_2$.

PHENYLMETHANES.

The homologues of benzene are of two kinds, as has been shown. They are obtained either by introducing one, two, or more methyl groups into benzene, or by introducing homologous residues of marsh-gas hydrocar-

bons into benzene. Just as methyl groups can be introduced into benzene, so also the group phenyl, C_6H_5, can be introduced into methane. Thus, the hydrocarbons are formed:—

Phenyl-methane,	$CH_3.C_6H_5$ (identical with toluene);
Diphenyl-methane,	$CH_2(C_6H_5)_2$;
Triphenyl-methane,	$CH(C_6H_5)_3$; and
Tetraphenyl-methane,	$C(C_6H_5)_4$.

Of the last three members, triphenyl-methane has been most carefully studied. It is the mother-substance of two important groups of compounds, the *aniline dyes* and the *phthaleins.*

The hydrocarbon is easily obtained by bringing chloroform, $CHCl_3$, and benzene, C_6H_6, together in the presence of aluminium chloride (reaction of Friedel and Crafts). In some way not understood, the chloride causes the two to act upon each other as represented in the equation

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$

Rosaniline and Pararosaniline.—The aniline dyes are for the most part comparatively simple derivatives of rosaniline or pararosaniline. Pararosaniline is formed by oxidizing a mixture of aniline, $C_6H_5.NH_2$, and paratoluidine, $C_6H_4\begin{cases}CH_3\\NH_2\ (p)\end{cases}$, as represented, thus:—

$$\underset{\text{Aniline.}}{2C_6H_7N} + \underset{\text{Toluidine.}}{C_7H_9N} + 3O = \underset{\text{Pararosaniline.}}{C_{19}H_{19}N_3O} + 2H_2O.$$

Rosaniline is formed in a similar way:—

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Toluidine.}}{2C_7H_9N} + 3O = \underset{\text{Rosaniline.}}{C_{20}H_{21}N_3O} + 2H_2O.$$

Pararosaniline has been made from triphenyl-methane by the following reactions which show the relations between the two compounds:—

By treatment with nitric acid the hydrocarbon yields a trinitro-derivative The same product is formed by bringing chloroform and nitro-benzene together in the presence of aluminium chloride, thus:—

$$CHCl_3 + 3C_6H_5(NO_2) = \underset{\text{Trinitro-triphenyl-methane.}}{CH(C_6H_4.NO_2)_3} + 3HCl.$$

By reduction the trinitro-product is converted into the corresponding triamido-derivative, $CH \begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{cases} = C_{19}H_{19}N_3$. By gentle oxidation this compound, known as *paraleucaniline*, is converted into pararosaniline. Pararosaniline has the constitution represented by the formula $C(OH) \begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{cases}$; or it is triamido-triphenyl carbinol. The salts of this compound are formed by addition of one molecule of the acid and elimination of one molecule of water. Thus the hydrochloric acid salt is formed according to this equation:—

$$C(OH) \begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{cases} + HCl = C \begin{cases} C_6H_4.NH_2 \\ C_6H_4.NH_2 \\ C_6H_4.NH.HCl \end{cases}$$

Similarly, rosaniline is represented by the formula

$$C(OH) \begin{cases} C_6H_3 < \begin{matrix} CH_3 \\ NH_2 \end{matrix} \\ C_6H_4.NH_2 \\ C_6H_4.NH_2 \end{cases}.$$

Its salts are analogous to those of pararosaniline.

Phthaleins.—The phthaleins are formed by treating a mixture of phthalic anhydride, $C_8H_4O_3$, and some phenol with a dehydrating agent. The simplest representative of the class is phenol-phthalein, which is made by heating a mixture of ordinary phenol and phthalic anhydride with sulphuric acid:—

$$\underset{\text{Phenol}}{2C_6H_6O} + \underset{\text{Phthalic anhydride.}}{C_8H_4O_3} = \underset{\text{Phenol-phthalein.}}{C_{20}H_{14}O_4} + H_2O.$$

The phthaleins are derivatives of triphenyl-methane, as has been shown by the following transformations:—

The chloride of phthalic acid, $C_8H_4O_2Cl_2$, when treated with benzene in the presence of aluminium chloride, yields a product known as diphenyl-phthalide:—

$$\underset{\text{Phthalyl chloride.}}{C_8H_4O_2Cl_2} + 2C_6H_6 = \underset{\text{Diphenyl-phthalide.}}{C_8H_4O_2(C_6H_5)_2} + 2HCl.$$

When boiled with sodium hydroxide, diphenyl-phthalide is transformed into an acid, triphenylcarbinol-carbonic acid:—

$$C_8H_4O_2(C_6H_5)_2 + H_2O = C_8H_6O_3(C_6H_5)_2 \text{ or } C_7H_5O \left\{ \begin{array}{l} COOH \\ (C_6H_5)_2 \end{array} \right.$$

When treated with zinc dust, this acid loses oxygen:—

$$C_7H_5O \left\{ \begin{array}{l} COOH \\ (C_6H_5)_2 \end{array} \right. + H_2 = C_7H_5 \left\{ \begin{array}{l} COOH \\ (C_6H_5)_2 \end{array} \right. + H_2O.$$

The product, triphenylmethane-carbonic acid, when distilled with baryta, loses carbon dioxide and yields triphenylmethane. It is hence to be regarded as a simple carboxyl derivative of triphenylmethane, $CH \left\{ \begin{array}{l} C_6H_5 \\ C_6H_5 \\ C_6H_4.COOH \end{array} \right.$.

In accordance with this conclusion, the other substances in the series must be represented by the following formulas: Triphenylcarbinol-carbonic acid,

$$C(OH) \left\{ \begin{array}{l} C_6H_5 \\ C_6H_5 \\ C_6H_4.COOH \end{array} \right. ; \text{ diphenyl-phthalide, } C \left\{ \begin{array}{l} C_6H_5 \\ C_6H_5 \\ C_6H_4CO \end{array} \right. .$$
$$\llcorner\text{——O——}\lrcorner$$

Phenol-phthalein is derived from the last compound by the introduction of two hydroxyls, and is represented by the formula

$$C \left\{ \begin{array}{l} C_6H_4.OH \\ C_6H_4.OH \\ C_6H_4.CO. \end{array} \right. = C_{20}H_{14}O_4 .$$
$$\llcorner\text{——O——}\lrcorner$$

Phenylethylene.—Ethylbenzene or phenylethane, $C_2H_5.C_6H_5$, can be converted into hydrocarbons containing two or four hydrogen atoms less, by means of the same reactions as those made use of for converting ethane into ethylene and acetylene. Thus, from ethane, bromethane is made, C_2H_5Br, and this, when treated with an alcoholic solution of potassium hydroxide, loses hydrobromic acid, yielding ethylene, $C_2H_5Br - HBr = C_2H_4$; and when dibromethane, $C_2H_4Br_2$, is treated in a similar way, it yields acetylene; $C_2H_4Br_2 - 2HBr = C_2H_2$. In like manner bromphenylethane, $C_6H_5.C_2H_4Br$, yields phenylethylene, $C_6H_5.C_2H_3$:—

$$C_6H_5.C_2H_4Br - HBr = C_6H_5.C_2H_3.$$

Phenylethylene is commonly called *styrene*. It is the mother-substance of the compounds of the indigo group. The relation of indigo-blue to this hydrocarbon has been established through the labors of Von Baeyer. Some of the derivatives are simpler and can be explained more easily.

Cinnamic acid has been shown to be phenylacrylic acid, $C_6H_5—CH{=}CH.COOH$, that is, it is the simple carboxyl derivative of phenylethylene, $C_6H_5—CH{=}CH_2$. When treated with nitric acid cinnamic acid yields two mono-nitroderivatives, one of which belongs to the ortho-series,

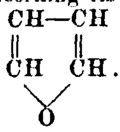
$$C_6H_5\left\langle\begin{matrix}C_2H_2.COOH\\NO_2\end{matrix}\right. .$$

This compound can easily be changed to indigo-blue, but the intermediate reactions are complicated.

When indigo-blue is oxidized it is converted into isatine, $C_8H_5NO_2$. A simple synthesis of isatine has been effected, which shows clearly what its constitution is.

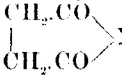
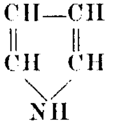
Orthoamidobenzoic acid, $C_6H_4\begin{cases}COOH\\NH_2\end{cases}$, yields a chloride, $C_6H_4\begin{cases}COCl\\NH_2\end{cases}$. The chlorine in this compound can be replaced by the cyanogen group, and the latter then converted into carboxyl. Thus, an acid, $C_6H_4\begin{cases}CO.COOH\\NH_2\end{cases}$, is obtained. This loses water very readily, and the anhydride thus formed, which is represented by the formula

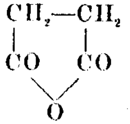
$$C_6H_4\begin{cases}C\,O.\,C\,O\\NH\,—\!\!\rfloor\end{cases},$$ is isatine.

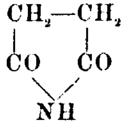
Furfuran.—Furfuran is formed from brompyromucic acid. It has the composition expressed by the formula C_4H_4O. Like benzene it forms addition products, and is therefore probably not saturated, just as ethylene and acetylene and their derivatives are unsaturated. It is not an alcohol nor an aldehyde nor a ketone. Taking all the facts known in regard to it into consideration, the most probable hypothesis suggested concerning its constitution is that expressed by the formula . This

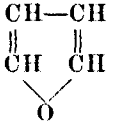
represents a compound similar to benzene in respect to the ring structure. It is benzene in which two of the CH groups have been replaced by an oxygen atom. Perfectly satisfactory proof of the correctness of this view has not been furnished, though the analogy between furfuran, pyrrol, and thiophene, the structure of which has been more thoroughly investigated, renders the view highly probable.

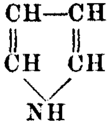
There are a number of derivatives of furfuran known, among which are *furfural*, $C_4H_3O.COH$, which is formed by the dry distillation of several of the carbohydrates, and *pyromucic acid*, $C_4H_3O.COOH$, which is formed by the dry distillation of mucic acid.

Pyrrol.—This compound with some of its homologues is found in bone oil and coal-tar oil. It is formed by the distillation of the ammonium salts of mucic and saccharic acids and by reduction of succinimide with zinc dust. One hydrogen in the compound evidently differs from the others, as only one is replaced by potassium when pyrrol is treated with this metal. Further, only one hydrogen is replaced by acetyl. These facts make it probable that pyrrol contains the imide group, and its formation by reduction of succinimide, , suggests the formula , according to which furfuran and pyrrol are analogous compounds, bearing to each other the same relation that succinic anhydride bears to succinimide:—

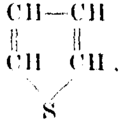

Succinic anhydride.


Succinimide.


Furfuran.


Pyrrol.

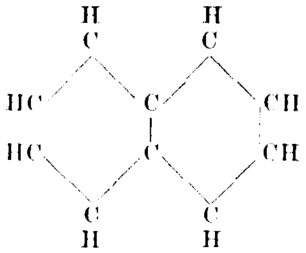
Thiophene.—In the benzene obtained from coal-tar oil there is contained a substance of the composition C_4H_4S, which is remarkably like benzene in all its properties; and its derivatives also exhibit the same resemblance to those of benzene. This is thiophene. The resemblance to benzene suggests at once that it probably has a similar constitution as represented in this formula,



According to this, thiophene is not only related to benzene, but to furfuran and pyrrol. The relation to furfuran and pyrrol is clearly shown by a number of reactions. There is a substance which, when treated with dehydrating agents, yields a furfuran derivative; when this same substance is treated with an alcoholic solution of ammonia it yields a pyrrol derivative; and when treated with phosphorus pentasulphide it yields a thiophene derivative. Further, thiophene is formed when succinic anhydride is treated with phosphorus pentasulphide; while, as was stated above, pyrrol is formed from succinimide by reduction. *The study of the isomeric substitution products* obtained from thiophene has only tended to confirm the formula above given. The existence of two isomeric mono-substitution products is indicated, and only two have been obtained, although many efforts have been made to make a third.

NAPHTHALENE.

The hydrocarbon naphthalene has the formula $C_{10}H_8$. It is considered to be formed by the union of two benzene residues in such a way that, while the compound contains the two residues, two of the carbon atoms are common to both residues. This is the fundamental idea in the prevailing view regarding the constitution of naphthalene. It is expressed thus:—



Assuming the formula for benzene to be correct, this is the only possible formula for naphthalene. It is based on the following facts: There is a derivative of naphthalene known as dichlornaphthoquinone, which has the formula $C_{10}H_4Cl_2O_2$. When this substance is oxidized, it yields phthalic acid, which is a di-substitution product of benzene. We see thus that those carbon atoms in dichlornaphthoquinone which are not in combination with chlorine form a benzene nucleus, so that we might write the formula of the compound $C_6H_4.C_4Cl_2O_2$. This formula does not tell us in what manner the atoms $C_4Cl_2O_2$ are united; but by the aid of another experiment this can be determined.

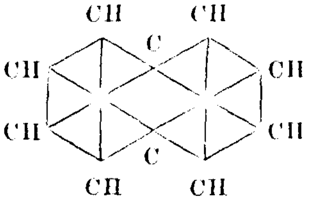
When dichlornaphthoquinone (the substance used in the preceding experiment) is treated with phosphorus pentachloride, it is converted into pentachlornaphthalene, the formula of which, according to what was said above, is $C_6H_3Cl.C_4Cl_4$. By analogy we should expect this compound by oxidation to yield monochlorphthalic acid; it, however, yields tetrachlorphthalic acid. This shows that the four carbon atoms which are in combination with the four chlorine atoms form part of a benzene ring, as well as the other carbon atoms of naphthalene. It is thus proved that in naphthalene there are two benzene rings. The only formula that agrees with this fact is the one above given.

The following facts lead to the same conclusion: Nitronaphthalene when oxidized yields nitro-phthalic acid. Therefore the part of the compound in which the nitro-group is contained is a benzene ring. When the nitro-compound is reduced amido-naphthalene is formed, and this by oxidation is converted into phthalic acid. It appears from this that there must be another benzene ring

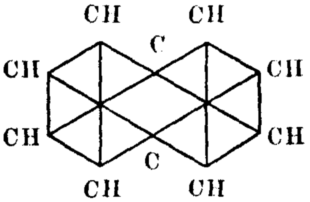
in naphthalene besides that in which the nitro- or amido-group is contained.

The derivatives of naphthalene resemble those of benzene, and much that has been said concerning the latter holds good in regard to the former. All the hydrogen atoms of naphthalene may be replaced by substituting groups or elements, and thus, as will readily be seen, a large number of substitution products can be obtained. The possibilities of isomerism are greater in the case of naphthalene than in the case of benzene, but the principles underlying the isomerism are essentially the same as those which have already been considered in connection with the isomeric substitution products of benzene.

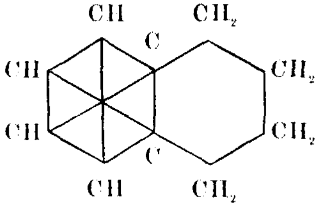
According to recent researches of Bamberger, naphthalene does not consist of two benzene rings, but it is so constituted that when addition to either of the rings takes place the other ring becomes a benzene ring. This conclusion is based upon elaborate investigations of the hydrogen addition products of naphthalene and its derivatives. Bamberger suggests that the constitution may be expressed by this formula:—



It will be seen that some of the bonds of the carbon atoms are directed towards the centre of the ring, but are not connected with the others which act in the same direction. It may fairly be asked whether the facts known warrant a distinction between the above formula and this:

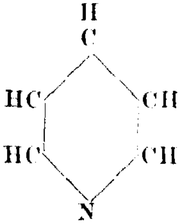


And to this question only a negative answer can be given. Taking the second form then, how does it explain the fact brought out by a study of the addition products of naphthalene? In the first place, it represents a compound consisting of two rings of the same constitution; second, these rings are not benzene rings; third, should addition take place to either ring the other ring would become a benzene ring, as shown in the formula below:



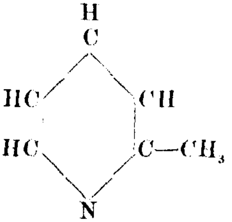
In this, the ring to the left has plainly the constitution of a benzene ring, as represented by Claus, and shown to be the most probable by Von Baeyer.

Pyridine and Quinoline.—A number of bases of the general formula $C_nH_{2n-5}N$ have been isolated from bone oil and made in other ways. The simplest one is pyridine, C_5H_5N. The others are homologous with it. Pyridine is a very stable compound, differing markedly in its chemical conduct from the common ammonium bases. By oxidation, its methyl derivatives yield corresponding carbonic acids, just as the analogous derivatives of benzene yield carbonic acids. For example: toluene or methyl benzene, $C_6H_5.CH_3$, yields benzoic acid, $C_6H_5.COOH$. So, also, picoline or methyl-pyridine, $C_5H_4(CH_3)N$, yields pyridine-carbonic acid, $C_5H_4N.COOH$, etc. While the facts known concerning pyridine are not sufficient to justify the expression of a very decided opinion regarding its structure, they nevertheless speak in favor of a structure similar to that of benzene. If one of the CH groups of benzene be replaced by a nitrogen atom, the resulting compound would have the forumla

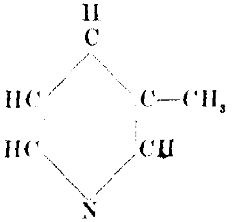


$= C_5H_5N$.

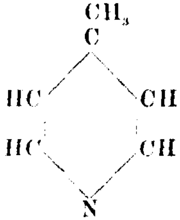
This formula represents the working hypothesis regarding the structure of pyridine. Thus far, the cases of isomerism studied are in accordance with this formula. There are, for example, three mono-methyl derivatives of pyridine, and three corresponding mono-carbonic acids. The formula suggests the existence of these three varieties. The three methyl derivatives are represented thus:—



Ortho-picoline.

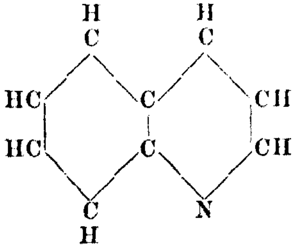


Meta-picoline.



Para-picoline.

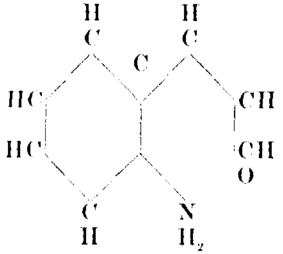
Quinoline, C_9H_7N, is the first member of a series of bases of the general formula $C_nH_{2n-11}N$, which somewhat resemble the pyridine bases. Quinoline is believed to bear a relation to naphthalene, similar to that which pyridine bears to benzene—a conception represented by the formula



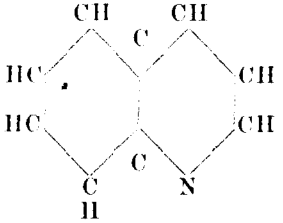
$= C_9H_7N$.

The method of preparation which perhaps most easily admits of interpretation is the following:—

Cinnamic aldehyde has the constitution represented by the formula $C_6H_5—CH = CH—COH$. The ortho-amido derivative of this aldehyde has the formula



This loses water easily and yields quinoline. As will easily be seen, the loss of water in the simplest way would lead to a substance of the formula

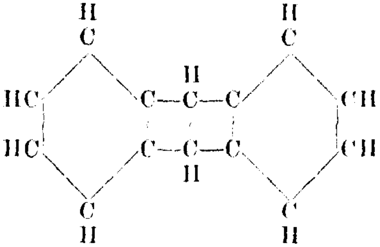


The question as to the structure of pyridine and of quinoline is intimately connected with the question as to the structure of benzene and of naphthalene. It is highly probable that, if the Claus formula for benzene is correct, all the other substances mentioned have a similar structure, though this does not necessarily follow.

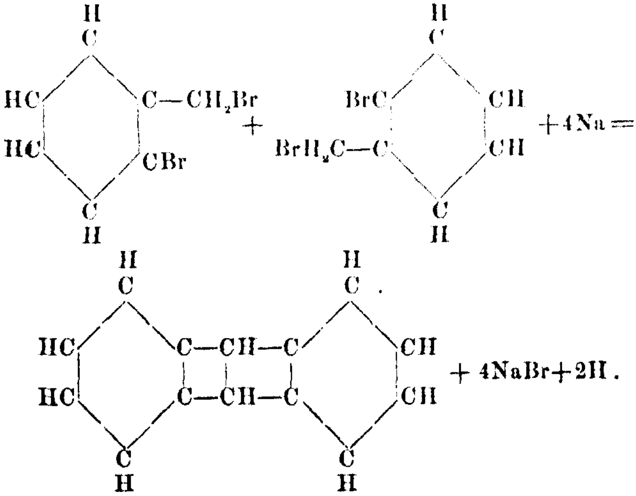
ANTHRACENE.

Anthracene, like naphthalene and benzene, is the mother-substance of a large group of compounds. Its formula is $C_{14}H_{10}$. In regard to its constitution, the view is held that

it consists of two benzene residues, C_6H_4, held together by means of the group $HC—CH$, each carbon atom of which is united to both benzene residues, thus:—



This formula is based, in the first place, on the similarity in the chemical conduct of benzene, naphthalene, and anthracene. Further, a synthesis of anthracene has been effected from orthobrombenzyl bromide, $C_6H_4\left\{\begin{matrix}CH_2Br\\Br\end{matrix}\right.$. When this compound is treated with sodium, one of the products is anthracene. The reaction may be represented thus:—



This reaction not only throws light upon the general character of anthracene, but it shows further that the linking groups CH are connected with the benzene residues in the ortho-position.

The formula given shows the relation between anthracene and anthraquinone, which appears to be

$C_6H_4 \left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle C_6H_4$. The latter formula best explains the formation of anthraquinone from benzoic acid, and the formation of benzoic acid from anthraquinone. The former transformation is represented thus:—

$$\begin{array}{c} C_6H_4 | H \;\; CO | OH \\ \times \\ C_6H_4 \, H | CO | OH \end{array} = C_6H_4 \left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle C_6H_4 + 2H_2O \, .$$

2 molecules Benzoic acid. Anthraquinone.

The formation of anthraquinone from anthracene should then be represented thus:—

$$C_6H_4 \left\langle \begin{array}{c} CH \\ | \\ CH \end{array} \right\rangle C_6H_4 + 3O = C_6H_4 \left\langle \begin{array}{c} CO \\ CO \end{array} \right\rangle C_6H_4 + H_2O \, .$$

According to these interpretations, anthraquinone is a double ketone. It has been suggested, further, that all quinones are double ketones. (See Quinones.)

Other hydrocarbons allied to naphthalene are pyrene, chrysene, and phenanthrene. These have not been investigated very fully as compared with naphthalene and anthracene themselves. All of these three undoubtedly contain benzene residues as essential parts of their molecules, but there is still some doubt in regard to the manner in which these residues are united.

Retrospect.

A study of the preceding chapters on constitution will show that no absolute meaning is to be attached to the word. Constitutional formulas are those which suggest cer-

tain reactions and recall analogies. The formula CH_3—OH does not mean that hydroxyl (OH) is necessarily present in the compound, or that CH_3 is present, but that the different parts of the compound bear such relations to each other that when the compound is decomposed it acts as if the parts were united as the formula indicates. The formula suggests possibilities; it may not represent realities.

The methods thus far considered for determining the constitution of compounds are chemical methods. They depend upon the study of chemical conduct. If we find that two compounds conduct themselves in the same general way, the formulas call this analogy to mind. If we assume a certain grouping in the one, we must assume a similar grouping in the other.

The question whether a study of the physical properties of compounds can throw any light upon the constitution of the compounds now naturally suggests itself. A great deal of attention has been paid to the subject of late, and a brief account of some of the methods employed and the results reached will now be given.

CHAPTER XVII.

PHYSICAL METHODS FOR THE DETERMINATION OF THE CONSTITUTION OF CHEMICAL COMPOUNDS.

General.—The study of chemical reactions makes it possible to determine the constitution of compounds in the sense in which the word constitution has been explained; that is, it makes it possible to draw conclusions in regard to the connections existing between the different atoms in molecules. The formulas expressing the results of the study are based upon a few fundamental conceptions in regard to the way in which molecules are made up. For example, the formulas of all the hydrocarbons of the methane series are based upon the conception that in the molecule of marsh-gas four atoms of hydrogen are combined in the same way with an atom of carbon, and the further conception that in ethane the two carbon atoms are in combination with each other and also with three hydrogen atoms each. Given these conceptions, and the theory of the whole series follows. The formulas of the members of the series are then the expressions in terms of the theory of the facts learned. Further, we find the same ideas underlying the prevailing views regarding the structure of all carbon compounds. So, too, when a number of compounds are represented by formulas in which double and triple lines occur, all that is meant by them is that those in which the double lines occur are like ethylene or carbon monoxide, and those in which the triple lines occur are like acetylene or the cyanides; and the question as to what the actual condition between the atoms is thus represented remains an open one. The same thing is true in regard to the benzene derivatives. By a thorough study of benzene a conception is formed in regard to the constitution of this compound. This conception is a result of an extension of the ideas already formed in studying the methane derivatives. Whenever a formula like that of benzene is seen it is recognized at once as the sign of the

benzene condition and the record of certain reactions. With the question of the *physical structure* of the molecules the views in regard to chemical constitution have nothing directly to do. Indeed, it does not appear probable that the study of chemical reactions alone, that is, of the decompositions and methods of formation of compounds, can ever lead to definite views in regard to the physical structure, if by physical structure be meant the arrangement of the atoms in space and the relations which they bear to one another in general. The only hope of gaining views upon this subject lies in a study of the physical phenomena attending chemical reactions, in an application of physical methods to the study of chemical problems. But the application of physical methods to the study of chemical problems will not necessarily touch the question of physical structure; and, indeed, the chief results thus far obtained in this field have simply had reference to the determination of a few points in connection with the chemical constitution. It has been found that in certain physical properties saturated compounds differ from unsaturated, and that, of the unsaturated compounds, those with double linkage differ from those with triple linkage. Therefore, by taking these differences into account, it is possible in some cases to determine whether a substance is saturated or unsaturated. Beyond this the application of physical methods has not advanced so far as the determination of constitution is concerned, except in a very few cases which will be referred to under thermal methods.

Specific Volume.—By the *specific volume* or *molecular volume* of a substance is meant a figure obtained by dividing the specific gravity of the substance in the form of liquid into the molecular weight. Thus, the specific gravity of ordinary alcohol at the boiling temperature is 0.736; the molecular weight is $24 + 6 + 16 = 46$; the specific volume is $\frac{46}{0.736} = 62.5$.

A study of the specific volumes of a large number of substances has shown that a close connection exists between the figures and the constitution of the substances. The specific gravities must be determined under strictly analogous conditions, in order that they may be comparable. The figures used are those found at the boiling-points

of the liquids. Kopp first pointed out that the following definite relations exist:—

1. *In many instances differences in specific volume are proportional to differences in corresponding chemical formulas.* Thus a difference of CH_2 in an homologous series corresponds to a difference of about 22 in the specific volume, or $(CH_2)\ x = 22\ x$. On comparing the specific volumes of haloid compounds of similar constitution, it is seen that the substitution of *n* atoms of bromine for an equal number of chlorine atoms increases the specific volume by $5n$.

2. *Metameric liquids have, as a rule, the same specific volume.* Exceptions are exhibited by certain oxygen and sulphur compounds.

3. *The substitution of an atom of carbon for two of hydrogen makes no alteration in the specific volume of members of certain groups of organic liquids.*

On the basis of his observations Kopp was able to calculate certain fundamental values for the specific volumes of the elements in combination. These values are, as a rule, constant for any particular element: thus, carbon has invariably the value 11; hydrogen, that of 5.5. Exceptions are observed in the case of the chemical analogues oxygen and sulphur. Each of these elements has two values, depending, it would seem, on its mode of combination, or on its relation to the remaining atoms in the molecule. For example: acetone and allyl alcohol have the empirical formula, C_3H_6O, but the specific volume of acetone is 78.2, whilst that of allyl alcohol is 73.8. As expressed in the ordinary formulas the affinities of the oxygen in acetone are wholly satisfied by the carbon, whereas in allyl alcohol a moiety of the combining value would seem to be satisfied by carbon, and the remainder by hydrogen. It appears, then, that when oxygen is united to an element by both its affinities its specific volume is 12.2; when it is attached by only one combining unit its specific volume is 7.8. The corresponding values for sulphur are 28.6 and 22.6.*

Assuming the conclusions of Kopp to be correct, a method is given for determining in what condition oxygen is present in a compound. An illustration will make the

* See Thorpe, Journal of the Chemical Society, xxxvii. 141.

application of the method clear. Suppose a compound of the formula C_2H_4O has the specific gravity 0.773. The specific volume is $\frac{44}{0.773} = 56.9$. Calculating the specific volume according to Kopp's rule, and accepting his values for carbon and hydrogen, viz., $C = 11$; $H = 5.5$, we have $V(C_2H_4O) = 2 \times 11 + 4 \times 5.5 + x$, in which x represents the specific volume of the oxygen. But the specific volume of the compound found by experiment is 56.9; hence we have $2 \times 11 + 4 \times 5.5 + x = 56.9$; $x = 12.9$.

The specific volume of oxygen in the compound under consideration is thus shown to be 12.9, or approximately the value assigned to oxygen combined with carbon by both affinities. Thus the presence of the group—CO—is proved by this method.

A thorough examination of all the facts on record bearing upon the subject of specific volumes has led Lossen to conclude that the rule of Kopp is not strictly true; that the specific volumes of the elements vary somewhat according to the class to which the compound into which they enter belongs. He considers it probable that certain figures will be found to express the specific volumes of the elements as they occur in different classes of compounds, and that these figures will be very similar to those given by Kopp. The whole subject of specific volumes is now under investigation.

Molecular Refraction.—The study of the refracting power of different organic liquids has led to results of interest, which show that there is a close connection between this power and the constitution of the compounds. In order that the results may be comparable the *refraction-equivalent* is determined. This is represented by the expression $P\left(\frac{n-1}{d}\right)$, in which P is the molecular weight of the compound, n the index of refraction, and d the density of the compound. The index is determined for four different lines of the spectrum obtained from the sodium light, and from the light emitted by hydrogen in a Geissler's tube.

Landolt has shown that, in general, substances of the same composition have the same refraction equivalent, the value of this equivalent being dependent upon the number and kinds of atoms present in a molecule, rather than upon the arrangement of these atoms. Each atom must then have its own refraction-equivalent, and, if this is known, the equivalent for a substance of any given composition

can be calculated. In order to determine the values for carbon, hydrogen, and oxygen, Landolt made use of several methods, the principle of which will appear from the following illustrations. Two compounds were compared with each other, the composition of which differed by one atom of carbon, two atoms of hydrogen, or one of oxygen, the difference in the molecular refraction of the two bodies giving the refraction-equivalent of the element. Thus, the refraction-equivalent ($P\frac{n-1}{d}$) of methyl alcohol is 13.17; that of aldehyde is 18.58. The difference in composition is one carbon atom. It is hence concluded that the difference in the molecular refraction of the two compounds is due to the one carbon atom, or that the atomic refraction of carbon is 5.41. In the same way aldehyde and ethyl alcohol, which differ in composition by two hydrogen atoms, show a difference in molecular refraction of 2.12; and it is concluded that the atomic refraction of hydrogen is half of 2.12. By comparing aldehyde and acetic acid, which differ by one atom of oxygen, the atomic refraction of oxygen is found to be 2.53.

		$P\left(\frac{n-1}{d}\right)$	*Difference.*
Difference in Composition C_1.			
Methyl alcohol,	CH_4O,	13.17	5.41
Aldehyde,	C_2H_4O,	18.58	
Difference in Composition H_2.			
Aldehyde,	C_2H_4O,	18.58	2.12
Ethyl alcohol,	C_2H_6O,	20.70	
Difference in Composition O_1.			
Aldehyde,	C_2H_4O,	18.58	2.53
Acetic acid,	$C_2H_4O_2$,	21.11	

As a mean of a large number of observations, the following values were obtained for the atomic refraction of the three elements:—

$$C = 5; \quad H = 1.3; \quad O = 3.$$

By means of these figures, then, the refraction equivalent of any given compound composed of these three elements can be calculated. On comparing the calculated values with those determined by experiment, Brühl found that the two are equal in a large number of cases, but that, in a number of other cases, the values found by experiment are greater than those calculated. More care-

ful examination of the subject showed that all the compounds that form exceptions to the general rule belong to the class of unsaturated compounds, and that all saturated compounds give results in harmony with the rule.

It was shown that:—

1. Univalent elements have a constant atomic refraction.

2. The occurrence in a compound of the condition known as double linkage between carbon atoms (see pp. 102 and 232) causes an increase of 2 in the value of the molecular refraction above that obtained by calculation.

3. The presence of carbonyl, CO, causes an increase in the molecular refraction above the value calculated for oxygen in the singly linked condition, as in C—O—H.

It is plain that, if these rules are well founded, a method is given for determining whether double linkage between carbon atoms, or between carbon and oxygen, exists in compounds under examination.

An application of this method to the study of the constitution of benzene led Brühl to the conclusion that there are three double bonds in this compound. He found that the molecular refraction is greater by 6 than that calculated with the use of Landolt's figures.

Methods dependent upon Determinations of the Amount of Heat Evolved in Chemical Reactions or Thermal Methods.—A fact which constantly impresses the observer of chemical phenomena is that every chemical change is accompanied by a change in temperature. In general the direct chemical combination of substances causes a rise in temperature, while decomposition involves an absorption of heat. For a long time chemists have been engaged in the study of the heat changes caused by chemical changes. The principal workers in this field have been Hess, Favre, and Silbermann, Berthelot, and J. Thomsen. The method of work consists in allowing known weights of substances to act upon each other in carefully constructed vessels called calorimeters, so that all the heat evolved or absorbed can be measured. The heat unit is the amount of heat necessary to raise the temperature of one gram of water one degree centigrade. This is called a calorie and is represented by the letter *c*. In stating the results of the thermo-chemical study of a reaction, the weights of substances taken into consideration are the number of grams

of each that correspond to their atomic or molecular weights. Thus the formation of water from hydrogen and oxygen is expressed by the equation :—

$$[H_2,O] = 68,360 \text{ c.}$$

This means that when 2 grams of hydrogen combine with 16 grams of oxygen the amount of heat evolved is 68,360 calories. It is obvious that observations on thermo-chemical reactions must be beset with difficulties. Generally other changes besides the chemical changes take place, and these cause thermal changes, and it is by no means a simple matter to decide what part of the total change is to be ascribed to the chemical changes. When, for example, two gaseous substances in combining give a liquid or a solid, the change from the gaseous to the liquid or solid state causes an evolution of heat, which is of course measured with that caused by the chemical combination, and, unless by special measurements the amount of heat thus evolved is determined, the thermo-chemical change proper is not known. Ingenious methods have been devised for getting over the difficulties, and for a large number of chemical reactions figures have been obtained of which it may be stated that they express analogous facts. While thermo-chemical studies have unquestionably been of benefit to chemistry and promise to be of greater benefit in the future, the generalizations reached in this line of work are not as yet of such character as to have a direct bearing upon most studies of chemical phenomena. This is partly, perhaps mostly, due to the fact that the prevailing hypothesis in regard to the constitution of chemical compounds and the nature of chemical reactions, although they are of the highest value and have been incalculably helpful to the science, are extremely crude when regarded from the mechanical point of view.

Heat of Formation.—Among the thermo-chemical measurements which have been made in largest number is that which is called the *heat of formation*. By this is meant the heat evolved in the formation of a compound. This heat of formation cannot, however, in most cases be measured directly, and must therefore be measured indirectly. Thus, for example, the heat of formation of marsh-gas cannot be measured directly. In such a case the measurement

is made as follows: The heat generated by the combustion of carbon is measured; then that generated by the combustion of hydrogen, and the two are added. It has been found that

$$[C,O_2] = 96,960 \text{ c.},$$
$$\text{and } 2\,[H_2,O] = 136,720 \text{ c.}$$

Therefore 233,680 c. is the heat of combustion of the constituents of a molecule of marsh-gas. Now the heat of combustion of marsh-gas itself is determined. As, in this operation, some of the heat evolved is used in separating the carbon and hydrogen, the heat of combustion of marsh-gas is less than that of its constituents. The following equation expresses the result of experiments:—

$$[CH_4,O_4] = 211,930 \text{ c.}$$

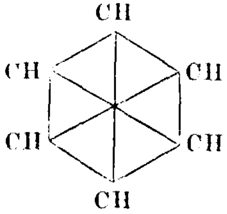
The difference between 233,680 c. and 211,930 c., which is 21,750 c., represents the amount of heat absorbed in separating the carbon from the hydrogen. But, as a result of a great many measurements the law has been established that *the heat absorbed in the decomposition of a substance is equal to the heat evolved in its formation*; and this law is also included in the general laws of the conservation of energy. Therefore, the heat of formation of marsh-gas is 21,750 c.

Thomsen has determined the heat of formation of a large number of hydrocarbons, and has attempted to interpret the results in terms of the valency-atomic hypothesis. It would lead too far to discuss here Thomsen's results in detail. Suffice it to say, he believes that by a study of the heat of formation of various hydrocarbons such as methane, CH_4, ethane, C_2H_6, ethylene, C_2H_4, acetylene, C_2H_2, propane, C_3H_8, and propylene, C_3H_6, it is possible, first, to draw a conclusion in regard to the heat evolved when a molecule of gaseous carbon C=C is formed, assuming that this molecule contains two atoms This is reached by a consideration of the heats of formation of—

$$2[C,H_4] = [C_2,H_8]$$
$$[C_2,H_6]$$
$$[C_2,H_4]$$
$$[C_2,H_2]$$

Between the thermal values of these reactions there is a

constant difference, and, assuming that the same difference holds good in passing to the next number of the series, viz., C_2, the heat of formation of this last member follows. Starting with these data and with the known heat of combustion of carbon and of carbon monoxide, values are obtained for the heat evolved when two carbon atoms unite by single linkage (v_1), by double linkage (v_2), and by triple linkage (v_3); and, further, a general formula is deduced for the heat of formation of hydrocarbons. In this formula the term Σ v enters. This represents the sum of the values v_1, v_2, v_3. This term is the unknown quantity. Knowing then the number of single, double, and triple linkages that occur in a hydrocarbon, it is possible to calculate the heat of formation; or, knowing the heat of formation, it is possible to determine the *number of single, double, and triple linkages* in the hydrocarbon. It is by an application of this method to benzene that Thomsen reached the conclusion that in this hydrocarbon there is no double linkage, but only single linkage, a conclusion which is in harmony with the formula



. The fact that this conclusion is directly opposed to that reached by a study of the refracting power of benzene admonishes us not to accept either without further investigation.

It will be observed that, even though this method were fully established, nothing material would be added to our knowledge of the structure of chemical compounds. The method would merely supplement the chemical methods already discussed, and enable us to classify hydrocarbons, and perhaps other carbon compounds, according to the prevailing chemical hypotheses.

Heat of Neutralization.—Studies on the *heat of neutralization* of acids and bases have led to some conclusions which may eventually prove of importance in connection with questions of structure. For example, Thomsen found

that the heat of neutralization of the first third of the hydrogen in phosphoric acid with caustic soda, and that of the second third are nearly equal, while that of the last third is much less. He, therefore, concluded that phosphoric acid is not, strictly speaking, a tribasic acid. If this conclusion is accepted, it ought to be taken into consideration in framing our views regarding the constitution of phosphoric acid. It may possibly be that the constitution should be represented by the formula $P \begin{cases} O-O-H \\ OH \\ OH \end{cases}$. Up to the present, however, the conclusions regarding structure reached by thermo-chemical studies are not generally accepted, when they conflict with those reached by purely chemical studies.

Other Conclusions.—Among other conclusions reached by Thomsen as a result of his thermo-chemical researches the following may be mentioned:—

1. The four affinities or bonds of the carbon atom are equivalent.

2. Pyridine and thiophene have no double linkages between the carbon atoms.

3. The so-called nitro-compounds of the paraffins, as nitromethane and nitro-ethane, do not contain the group NO_2.

4. The heat of formation of the amines indicates that the amines of the fatty series and those of the aromatic series have not the same constitution.

5. The aldehydes contain the group $-\overset{|}{\underset{|}{C}}-O-H$, and are represented by the general formula $R-\underset{\|}{C}-O-H$, being unsaturated.

It will be seen that there is a general lack of harmony between the results obtained by thermo-chemical methods and those obtained by strictly chemical methods Of course, the difficulty is simply in the interpretation of the facts. The facts themselves cannot be disturbed.

Magnetic Rotary Polarization in Relation to Chemical Constitution.—The fact that when polarized light passes through a substance placed in a magnetic field its plane is

rotated was discovered by Faraday. Recently W. H. Perkin* has shown that there is a definite relationship between the magnetic rotary power of substances and their chemical constitution. The effect upon polarized light in a magnetic field produced by lengths of columns of liquids related to each other in proportion to their molecular weights was measured, and this effect compared with the effect produced by water; thus figures were obtained that could be compared with one another. The result for each case is represented by the simple formula $\frac{r + Mw}{d}$, in which r is the rotation observed, Mw the molecular weight, and d the specific gravity. By dividing the result in the case of the substance under examination with that in the case of water, the figure called the "molecular coefficient of magnetic rotation," or the "molecular rotary power," is obtained.

Among the results thus reached bearing upon the question of chemical constitution the following may be mentioned:—

The effect of an addition of CH_2 to a compound is to increase its molecular magnetic rotation by 1.023. With this result it is possible to calculate the molecular rotation of any member of an homologous series, if that of one member is known. Take œnanthylic acid, $C_7H_{14}O_2$, as an example. Subtract 7 × 1.023 from its molecular rotation, and there is left a residue in excess of that which the product would give if it consisted of CH_2 only, thus:—

Molecular rotation of œnanthylic acid . .	7.552
1.023 × 7	7.161
Difference	0.391

This residual number is called the *series constant*, and is designated by *s*. Thus a formula for the acids of this series may be constructed: $C_nH_{2n}O_2 = 0.391 + n(1.023)$.

Similarly, formulas for the magnetic rotary power of other classes of compounds can be constructed, as for ethereal salts, paraffins, aldehydes, etc.

The normal and isomeric compounds of a series give different figures. The isoparaffins may be regarded as

* For details see Perkin's Memoir in the Journal of the Chemical Society (London), 1884, p. 421.

normal paraffins in which an atom of hydrogen in the CH_2 group already associated with methyl has been displaced by methyl, thus:—

$CH_3.CH_2.CH_2.CH_3$. Butane.	$(CH_3)_2CH.CH_2.CH_3$. Methyl-butane or isopentane.
$CH_3.CH_2.CH_2.CH_2.CH_3$. Pentane.	$(CH_3)_2CH.CH_2.CH_2.CH_3$. Methyl-pentane or isohexane.

The influence of the introduction of methyl on the molecular rotation is very marked, as it increases the rotation to a greater extent than would result from the change in composition caused by the introduction of CH_2.

Again, it was found that the introduction of carboxyl causes a reduction in the magnetic rotation of alcohol radicals when associated with it, although the rotation of the group itself is evidently high.

As regards the effect of hydroxyl it was found that, both in the series of the paraffins and the aldehydes, the introduction of hydroxyl in place of hydrogen increases the molecular rotation.

On comparing the molecular rotation of a paraffin with that of the corresponding aldehyde and acid, it was found that oxygen, when displacing two hydrogens on the same carbon, has nearly double the influence that it has when simultaneously combined with hydrogen and carbon.

Unsaturated compounds show a larger molecular rotation than the corresponding saturated compounds.

It will be seen from the above that, by making observations on the magnetic rotation of substances, it is possible to draw certain conclusions regarding their chemical constitution.

The Shape of Molecules.—The methods of study thus far discussed do not touch the question as to the shape of molecules and the arrangement of the atoms in space. In the common language of chemistry we speak of chain-shaped molecules, of chains with branches, of rings and double rings, and we make constant use of the hexagon in representing the structure of benzene and its derivatives. But, as has been repeatedly stated, these expressions refer to the formulas, and the formulas refer to facts that have no necessary connection with space relations. While we represent the symmetry of benzene by means of a circle or a regular hexagon, we know that the atoms

in the molecule of benzene cannot be arranged in a plane. But, as we know nothing or very little concerning the arrangement in space, we wisely refrain from attempting to express anything concerning it in our formulas. When the physicist says let the line A——B represent a force he can hardly be accused of thinking that the line is a picture of the force. He knows that he represents certain properties of the force, viz., magnitude and direction, in regard to which he has knowledge, and the use of this sign is of great assistance in enabling him to deal with a certain order of facts. So, too, the chemist can fairly represent the facts with which he has to deal by means of symbols, and, if rightly used, they are of great assistance to him. Still, though the consideration of space relations may be postponed because of a lack of facts upon which to base a plausible hypothesis, the problem nevertheless remains to be solved. Some efforts have been made to reach conclusions regarding the subject, and of late these have produced a marked effect upon the science.

One of the results reached may be stated thus: It is shown that the boiling points, densities, and indices of refraction vary in the same way; that for isomeric compounds the constants of that one are largest which consist of an uninterrupted chain of hydrocarbon residues, and that the constants become smaller the more the structure of the molecule is branched, and deviates from one direction. The data thus far established seem to show that the shorter the molecule of isomeric compounds, *i. e.*, the more they approach the spherical form, the larger is the molecular volume.*

The words "shorter," "branched," etc., used in the above statements, have primarily, of course, reference to the appearance of the formulas in common use. Assuming that these formulas do in a crude way represent the actual shapes of the molecules, there probably exists a direct connection between the variations in the physical constants of isomeric compounds and the actual shape of the molecules.

Thus, the specific gravity of compounds with long molecules would necessarily be greater than that of compounds with branched or spherical molecules, for the same reason

* Brühl, Annalen der Chemie, Vol. 203, p. 363.

that we can get more rods in a given space than spheres of the same weight. So, also, with reference to the boiling point. The rod-shaped molecules offer the most points of contact, the spherical the least. The adhesion between molecules of the first kind will hence be the greatest, and the conversion of the substances into vapor will be more difficult than is the case with other substances, or the boiling points will be higher. Similar considerations indicate that the facts observed in connection with the time of transpiration of vapors are in harmony with the view that the usual formulas represent to some extent the general shape of the molecules.

The most important speculations bearing upon the question of the space-relations of atoms are based upon the existence of such cases of isomerism as those exhibited by the lactic and tartaric acids and some other similar ones.

A study of the effects produced upon polarized light when it passes through certain chemical compounds has led Le Bel and van't Hoff to propose an hypothesis in regard to the arrangement of atoms in the molecules of these compounds. Reference has already been made to this hypothesis (see *ante*, p. 220) to account for some cases of isomerism which cannot otherwise be explained. Thus there are three lactic acids, which, according to all we know regarding their methods of formation and their chemical transformations, must be represented by the same ordinary chemical formula $CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-COOH$. While these substances are very similar in all other respects, they differ in their effects upon polarized light. One, ordinary lactic acid, has no perceptible effect upon polarized light; another, paralactic acid, turns the plane of polarization to the right, while the third turns it to the left. Further, there are three acids, dextro-tartaric and lævo-tartaric acids, and racemic acid, all of which appear to have the same structure, as far as our formulas express structure. One of these turns the plane of polarization to the right, another turns it to the left, while racemic acid is optically inactive. These facts can be explained according to the hypothesis as follows: Let it be supposed that in a carbon compound

one carbon atom is situated at the centre of a tetrahedron, and that the four atoms or groups which it holds in combination are at the angles of the tetrahedron, as represented in Fig. 1. If all these groups are different in kind, *and only in this case*, it *is possible to arrange them in two* ways with reference to the carbon atom. The difference between the two arrangements is that which is observed between either one and its reflection in a mirror. Imperfectly the second arrangement of the figure is represented in Fig. 2.

Fig. 1.

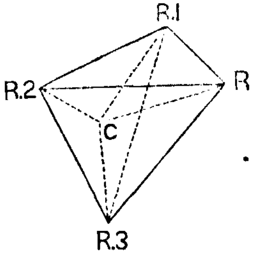
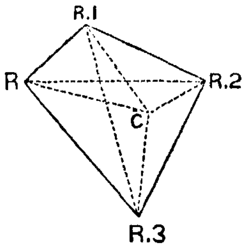


Fig. 2.



A carbon atom, in combination with four different kinds of atoms or groups, is called an *asymmetrical carbon atom.* Whenever, therefore, a compound contains an asymmetrical carbon atom, there are two possible arrangements of its parts in space which correspond to the complementary tetrahedrons, viz., the right-handed and the left-handed tetrahedron. The third, optically inactive modification of a substance, is believed to be a molecular compound of the other two. In the lactic acids and in the tartaric acids the asymmetrical carbon atom is present, as is shown by the formulas:—

$$\begin{array}{c} H \\ | \\ CH_3—C—COOH \\ | \\ OH \end{array} \qquad \begin{array}{c} H \\ | \\ HO—C—COOH \\ | \\ HO—CH.COOH \end{array}$$

Lactic acid. **Tartaric acid.**

In lactic acid the central carbon is in combination with 1)OH; 2)COOH; 3)H; and 4)CH_3. In tartaric acid the

four different groups and atoms are 1)H; 2)COOH; 3) CH.COOH; and 4)OH.

While a great deal more work is necessary before this hypothesis can be regarded as completely established, our knowledge on the point at present may be fairly summed up in the following sentences:—

1. Optically active substances always contain one or more asymmetrical carbon atoms.

2. Substances which do not contain asymmetrical carbon atoms have no rotary power.

According to this hypothesis, the affinities of an atom are exerted in definite directions, *i. e.*, towards the angles of a tetrahedron at the centre of which the carbon atom is supposed to be. Von Baeyer has attempted to show that, on this assumption, the fact that rings of six carbon atoms are easily formed and are stable, finds a plausible explanation. This will be easily understood if we conceive the affinities to be lines extending from the carbon atoms in the direction indicated. When six carbon atoms are *brought together they can combine if the direction of* their lines be changed only very slightly; while, in the case of four or five carbon atoms, the displacement would be considerable, and, as Von Baeyer expresses it, the tension would be so great that the compound would be unstable. What value to attach to such considerations at present it is difficult to say. In this, as in so many other cases in which our knowledge is imperfect, we can only wait until further work shall have furnished us with more facts.

That branch of chemistry which has to deal with the phenomena of space relations is known as *stereochemistry*. Within the last few years there has been great activity in this branch, and it seems highly probable that more and more attention will be given to it, as the results already reached are of great interest.

CHAPTER XVIII.

THE STUDY OF CHEMICAL AFFINITY.

Introduction.—Our study thus far has been confined to questions of composition and constitution, and, indeed, as already stated, originally the main object of this book was to discuss the facts upon which the prevailing views regarding constitution are based. One cannot, indeed, overestimate the value of the work that has been done in the way of investigating chemical constitution. The widespread applicability of the prevailing views to the interpretation of chemical phenomena, the brilliant successes that have been achieved in the building up of complex compounds by methods suggested by these views, furnish overwhelming evidence of the truth there is in them. A complete study of chemistry, however, involves not only the subject of constitution, but that of the nature of chemical action itself. We should not be satisfied with studying chemical compounds after they are formed, but we must, if possible, make observations *during the act* of formation, and thus get as much insight as possible into the nature of the act. For various reasons there are serious difficulties in the way of such observations, and, although a great deal of work of the kind indicated has been done, the results up to quite recently have not been of special importance.

The Nature of the Problem.—We know that when hydrogen and chlorine are brought together they combine with great evolution of heat. The act is generally instantaneous and it is therefore practically impossible to make any observations during its consummation. In the smallest particle of the resulting gas both hydrogen and chlorine are found in definite proportions; and in order to separate them or to decompose the compound, an expenditure of energy is necessary. The phenomenon suggests

such phenomena of attraction as those of gravitation, electricity, and magnetism. We, therefore, picture to ourselves the atoms of hydrogen and chlorine as drawn together by an attractive force, much as the stone thrown upwards is drawn to the earth or as the electrified body is attracted by other bodies. In each case to separate the attracted substances an expenditure of energy is necessary. Without any conception in regard to the nature of this chemical force we may for convenience call it *chemical affinity*. The first object in view in the study of this force is to measure its intensity in different cases. What is the difference between the attraction exerted between hydrogen and chlorine and that exerted between hydrogen and oxygen, etc. etc.? Is it dependent on the nature of the substance, or is it independent of the nature and only dependent on the mass? Such are some of the questions that suggest themselves. What we want is a measurement of the attractive force exerted between the atoms of all the elements under different conditions. It is plain that with this knowledge we should be in a position to predict in every case the exact character of the reaction or reactions between any substances. Let us see what progress has been made in this line.

Rough Measurements of Affinities.—It has long been known that some elements combine with ease, and form stable compounds, while others combine with difficulty and form unstable compounds, and others still do not combine at all, and of these elements it has been said that those of the first class have a *strong* affinity for one another, those of the second class have a weak affinity for one another, and those of the third class have no affinity for one another. Thus hydrogen and oxygen, phosphorus and oxygen, potassium and oxygen, etc. etc., have a strong affinity for each other; nitrogen and hydrogen, carbon and hydrogen, chlorine and iodine, etc. etc., have a weak affinity for each other, and fluorine and oxygen, chromium and hydrogen, etc. etc., have no affinity for each other. Further, in certain natural groups of elements a gradation in affinity in accordance with the gradations in the atomic weights is easily recognized, as, for example, in the group of the so-called halogens, chlorine is said to be a stronger element than bromine, and bromine a stronger element

than iodine. These statements are based upon observations on the action of chlorine on compounds of bromine and iodine. As chlorine decomposes the compounds of these two elements, it is said to be a stronger element, by which is meant that it has a stronger affinity towards other elements. Hosts of similar observations have been made, and it is generally recognized that chemical reactions take place in consequence of differences in the affinities of the elements for one another. If, for example, the elements A and B have for each other the same affinity as C and D, and this is the same as the affinity of A for D, A for C, B for C, and B for D, then, on bringing the compounds AB and CD together, no change takes place; but if the affinity of A for C is greater than that of A for B, and that of C for D greater than that of B for C, then the change represented in the equation,

$$AB + CD = AC + BD$$

will take place.

By careful observations of chemical reactions, then, it is possible to get some idea regarding the relative strength of the affinities of the elements, but much more refined methods are necessary.

Disturbing Influences.—A serious difficulty in the way of measuring affinity by chemical observations is found in the fact that decompositions do not always take place in accordance simply with the strength of the affinities of the elements which take part in the reaction; and, indeed, this is markedly true of those reactions which we most frequently have to deal with. The most common disturbing causes are changes in the state of aggregation of the forms of matter. Thus, when by adding a substance A to a substance B, a substance C, which is a gas at the temperature employed, can be formed, then in general the gas will be formed, each particle escaping as soon as formed, and thus being removed from the sphere of action. An example of this kind is furnished by the decomposition of a chloride or a nitrate by sulphuric acid. In each case with the aid of slight elevation of temperature there is decomposition, and finally there is complete replacement of the hydrochloric or nitric acid by sulphuric

acid. From this the conclusion is frequently drawn that sulphuric acid is a stronger acid than the other two. But all methods of comparing these acids under the same conditions show that hydrochloric and nitric acids are, as a matter of fact, much stronger acids than sulphuric acid, and the cause of decomposition of the nitrates and chlorides by sulphuric acid is to be found in the fact that volatile products are formed. Again, when a product of the reaction of two substances in solution is an insoluble solid, *the decomposition will generally take place and be complete*, independently of the strength of the affinities. The affinity of chlorine for sodium is greater than that of chlorine for lead; but, if to a solution of sodium chloride a solution of lead acetate be added, lead chloride is thrown down, though not completely. *Here, as in the case of the formation of* a volatile product, the product is removed from the sphere of action as soon as formed, and this causes an entire change of the process.

From these examples it will be clear that the simple fact that one substance, *A*, decomposes another, *BC*, and unites with *C* to form *AC*, is not sufficient evidence that the affinity of *A* for *C* is greater than that of *B* for *C*. This is especially the case when the product, *AC*, is a gas or an insoluble solid.

Attempts to measure Affinity by Observations on the Heat evolved in Chemical Reactions.—If a mass of hydrogen and a mass of chlorine consisted of isolated atoms at rest, and, after the combination, the molecules as well as their constituent atoms were at rest, then the heat evolved in the act of combination would be the result of the transformation of the potential energy of the atoms into kinetic energy, and it would be a measure of the affinity exerted between the atoms. But not one of these conditions can be assumed with any confidence, and most of them are undoubtedly not true. We have abundant evidence to show that the mass of hydrogen and that of chlorine do not consist of isolated atoms. Taking then the reaction between hydrogen and chlorine, it is clear that it is not simply a combination of atoms, but that the act of combination between the atoms must be preceded by the decomposition of the molecules of hydrogen and

those of chlorine. According to our present views, the reactions must be represented in this way:—

$$(1)\quad H_2 + Cl_2 = H + H + Cl + Cl\,;$$

$$(2)\quad H + H + Cl + Cl = HCl + HCl\,.$$

The heat which is evolved in the reaction is therefore not simply the result of the combination of hydrogen and chlorine, but it is this heat less that which is used in decomposing the molecules of hydrogen and of chlorine into atoms. The heat measured is the difference between two quantities; and we have no way of estimating the value of these quantities. This is true of every chemical reaction. The heat evolved or absorbed in the reaction is the difference between two or more quantities, and it is not, therefore, a measure of affinity.

Nevertheless, some knowledge regarding the relations which the affinities of elements bear to one another can be gained by a study of the heat evolved in their reactions. Thus, the following results have been obtained in the study of chlorine, bromine, and iodine:—

$$[H_2,Cl_2] = 2[H,Cl] - [H,H] - [Cl,Cl] = 44{,}000\ c.$$

$$[H_2,Br_2] = 2[H,Br] - [H,H] - [Br,Br] = 16{,}880\ c.$$

$$[H_2,I_2] = 2[H,I] - [H,H] - [I,I] = -12{,}072\ c.$$

The figures thus obtained are not proportional to the affinities of chlorine, bromine, and iodine to hydrogen, but, nevertheless, the affinities in all probability vary in the same order.

The difficulties are much increased in more complicated cases, and it will therefore be seen that it is impossible to measure the affinity between atoms by means of the heat evolved in reactions.

Resultant Affinity.—While affinity in the strictest sense must be regarded as a simple force acting between atoms, yet we may speak of the affinity of one molecule for another, meaning by the expression the resultant of the various atomic affinities which are brought into play when the two molecules combine. This resultant affinity is of course a complex quantity, as has been pointed out. Nevertheless, it is desirable to make as many measurements of it as possible. The meaning of the term will be

clear by a reference to the cases of chlorine, bromine, and iodine. The measurements recorded in the last paragraph represent the resultant affinities of these elements to hydrogen in terms of heat units. In a similar way we may speak of the resultant affinities of acids and bases towards one another. Thus the resultant affinity of hydrochloric acid towards caustic soda involves the following reactions:—

$$(1)\ H—Cl + Na—O—H = H + Cl + Na + (O—H).$$

$$(2)\ H + Cl + Na + (O—H) = Na—Cl + H—O—H.$$

Notwithstanding the complex character of measurements made in such cases they are of service in dealing with chemical questions.

Heat of Neutralization.—Acidity of Acids.—Among the measurements that have proved of value in connection with the study of the general problem of affinity are those furnished by the heat of neutralization of acids and bases. This subject has been investigated very extensively by Thomsen. The general method of work consisted in determining the heat evolved when equivalent quantities of different acids are neutralized by the same base, and equivalent quantities of different bases are neutralized by the same acid. Knowing the heat evolved in the reactions between the various acids and bases, it is possible to learn something in regard to what takes place when acids act upon salts in those cases in which decomposition is not evident. Thus, when nitric acid acts upon sodium sulphate in solution, several changes are possible, as represented in the equations:—

$$(1)\ Na_2SO_4 + HNO_3 = NaHSO_4 + NaNO_3;$$

$$(2)\ Na_2SO_4 + 2HNO_3 = H_2SO_4 + 2NaNO_3;$$

$$(3)\ 2Na_2SO_4 + 4HNO_3 = Na_2SO_4 + 2NaNO_3 + H_2SO_4 + 2HNO_3.$$

As all the substances involved in these reactions are soluble in water, and the reactions are studied in water solution, it is clear that by ordinary methods it would be impossible to tell which of them take place. By thermochemical methods, however, it has been shown that in this and in all similar cases the base is divided between

the two acids and generally more goes to one acid than to the other. Further, it is possible to measure the *division of the base between the acids*, and in this way measurements of the relative strengths of the acids are obtained. The figures representing the strengths of the acids measured in this way are called by Thomsen the *avidities of the acids*. In the case taken as an illustration it was found that in dilute aqueous solution two-thirds of the soda combines with the nitric acid and one-third with the sulphuric acid. Therefore, it appears that the avidity of nitric acid is twice as great as that of sulphuric acid. Of all acids investigated nitric and hydrochloric acids were found to have the greatest avidity. Calling this 1.00, the avidities of some other acids are represented in the following table:—

Acids.			Avidity.
1	Mol.	Nitric acid	1.00
1	"	Hydrochloric acid	1.00
1	"	Hydrobromic "	0.89
1	"	Hydriodic "	0.79
½	"	Sulphuric "	0.49
½	"	Selenic "	0.45
1	"	Trichloracetic "	0.36
1	"	Orthophosphoric acid	0.25
½	"	Oxalic acid	0.24
1	"	Monochloracetic acid	0.09
1	"	Hydrofluoric "	0.05
½	"	Tartaric acid	0.05
⅓	"	Citric "	0.05
1	"	Acetic "	0.03
½	"	Boric "	0.01
½	"	Silicic "	0.00
1	"	Hydrocyanic acid	0.00

It is impossible to give an exact interpretation of these results, but it appears that the figures given represent the numerical relations between some common property possessed by acids, a property which we have vaguely in mind when we speak of the strength of acids. This appears more clearly when acids and bases are studied by other methods.

Mass-Action.—At the beginning of this century appeared C. L. Berthollet's *Essai de statique chimique.* The author took the ground that chemical affinity is essen-

tially the same as gravitation. If this be true, however, chemical action must be proportional to the masses of the substances acting upon each other. This carries with it another conclusion, viz: That when a substance AB is decomposed by CD with the formation of AC and BD, the action will grow less and less, as the masses of the original substances decrease, and, finally, a stage will be reached before the decomposition is complete when no further action will take place, or a state of equilibrium will be established between the four substances. Berthollet's fundamental proposition is this:—

"Every substance which tends to enter into combination acts in proportion to its affinity and its mass."

Not much attention was paid to the work of Berthollet until recently. Now, especially through the labors of Guldberg and Waage and of Ostwald, the truth of this fundamental proposition has been established and the study of affinity has been materially advanced.

In 1852 Rose published a paper on the action of water on various chemical compounds and showed that there is some connection between the quantity of water used and the extent of the decomposition. A little later Bunsen showed that, when to a mixture of hydrogen and carbon monoxide not enough oxygen is added to oxidize the gases completely, the oxygen is divided between the two gases *not in proportion to their quantities, but so that the quantities* of carbon dioxide and water produced stand in simple rational ratio to each other. This result was afterward shown to be erroneous by Horstmann. Many observations made since have shown that the extent of a chemical reaction is unquestionably influenced by the mass of the substances brought into action.

The important papers of *Guldberg* and *Waage* appeared in 1867 and later. The starting-point of their investigations will appear from the following quotation:—

"When two substances *A* and *B* are transformed into two new substances, *A'* and *B'*, the chemical force with which *A* and *B* act upon each other is measured by the quantity of the new substances formed in unit time."

"The quantity of a substance in unit volume of the compound in which the chemical change takes place we call the *active mass* of the substance."

"The chemical force with which two substances, *A* and

B, *act upon each other is equal to the product of their active masses, multiplied by the coefficients of affinity*."

"By coefficient of affinity a coefficient is understood which is dependent upon the chemical nature of the two substances and upon the temperature. If the active masses of A and B are represented by p and q and the coefficient of affinity by k, then the force acting between A and B is expressed by kpq. . . ."

"When in a chemical process A and B are transformed into A' and B', and A' and B' can at the same time be transformed into A and B, equilibrium will be established when the force acting between A and B is equal to the *force acting between* A' *and* B'."

"If the active masses of A' and B' be represented by p' and q' and their coefficient of affinity by k', the chemical force acting between A' and B' is expressed by $k'p'q'$."

"The condition of equilibrium is therefore expressed by the equation $kpq = k'p'q'$."

The above statements taken together form the *law of mass-action*. The law as thus stated can be tested and has been tested by the authors in a number of ways and found to hold true.

Measurement of Coefficients of Affinity.—The law of mass-action as stated makes it possible to measure what Guldberg and Waage call the coefficients of affinity in cases where reversible reactions of the kind above referred to take place, or at least to measure the ratio between the two coefficients involved. Thus, in the equation

$$kpq = k'p'q',$$

p, q, p' q' represent the number of equivalents of the four substances which take part in a reversible reaction. If these are known, it is clear that the ratio $\frac{k}{k'}$ is also known.

An example of the application of this method is furnished by the case of the action of alcohol on acetic acid studied by Berthollet and St. Gilles. When these substances are brought together the formation of acetic ether begins, but after a time stops. At first the reaction

$$CH_3.COOH + C_2H_5OH = CH_3.COOC_2H_5 + H_2O$$

takes place. But the substances formed also act upon

each other to some extent in the reverse way. It was found that when

$$\text{acid} + \text{alcohol} = \tfrac{1}{4} (\text{ether} + \text{water})$$

the action stopped or equilibrium was established, or, in this case, $\frac{k}{k'} = \frac{1}{4}$. It was further found that by changing the proportions of the substances the quantity of ether formed was changed, and the quantity formed agreed with that calculated by means of the equation of equilibrium when $\frac{k}{k'} = \frac{1}{4}$.

Later it was shown that the results obtained by Thomsen in his studies on neutralization are in perfect accordance with the theory of Guldberg and Waage; what Thomsen calls the avidity of acids and bases being the same as the coefficient of affinity.

Velocity of Chemical Change as a Means of Measuring Coefficients of Affinity.—The coefficient of affinity may, according to Guldberg and Waage, be measured by determining the velocity of chemical changes. Their first proposition (see *ante*) is:—

"When two substances, *A* and *B*, are transformed into two new substances, *A'* and B', the chemical force with which *A* and *B* act upon each other is measured by the quantity of the new substances formed in unit time."

The force tending to bring about the reaction is represented by $k\,p\,q$, and since the velocity is proportional to the active force we have

$$v = \phi (k\,p\,q)$$

in which ϕ is the coefficient of velocity. This equation holds for reactions which proceed in one direction only. When the reaction is reversible the total velocity will be equal to the difference between the velocities in opposite directions, or

$$v = \phi(k\,p\,q - k'\,p'\,q').$$

This conception has been tested in a number of reactions. Among them that of the action of water on acetamide, and that of water on methyl acetate have been studied by Ostwald, with the result of showing it to be well founded.

Volume-chemical Method.—Ostwald has tested the law of mass-action by means of observations on specific gravities of solutions, and has in this way reached conclusions regarding the relative affinities of some acids. The method depends upon the fact that chemical processes which take place in homogeneous liquids generally cause changes in volume. "Thus, the specific gravity of a normal caustic soda solution was found to be 1.04051, that of an equivalent solution of sulphuric acid 1.02970, that of an equivalent of nitric acid 1.03089. When equal volumes of soda solution were mixed with each of the acids, the specific gravity of the sodium sulphate solution was 1.02959, and that of the nitric solution 1.02633. Finally, when to the solution of sodium sulphate (2 vol.) one equivalent (1 vol.) of nitric acid was added the specific gravity became 1.02781."* By means of these figures it is possible to determine to what extent the nitric acid acts upon the sulphate, and thus to draw conclusions regarding the distribution of the base between the acids. This, it will be observed, is another method of solving the problem which was attacked by Thomsen by thermo-chemical methods. The results reached by the volume-chemical method agree in general with those reached by the thermo-chemical method.

Specific coefficient of Affinity.—According to Guldberg and Waage the coefficient of affinity, k, in the equations already explained, is a coefficient dependent upon the chemical nature of the two substances that enter into action and upon the temperature. But this coefficient must be the product of two *specific coefficients of affinity*, one belonging to one substance and the other to the second substance. By investigating the action of a number of bases on one acid, and of a number of acids on one base by different methods, Ostwald found that the relative affinity of acids is independent of the nature of the base, and that the relative affinity of the base is independent of the nature of the acid. Each acid and each base has a specific coefficient of affinity, and the affinity of any acid for a base is the product of the specific coefficient of affinity of the acid and the specific coefficient of affinity of the base. On comparing the figures representing the specific coeffi-

* See Ostwald, Allgemeine Chemie.

cients of affinity of the acids with the figures obtained by Thomsen, and called by him the avidities of the acids, the two are found to bear approximately the same relation to one another.

Methods for Determining Specific Coefficients of Affinity.—The volume-chemical method was supplemented by Ostwald by several other methods which enabled him to determine the relative influences exerted by a number of acids under a variety of circumstances. Among other methods may be mentioned the optical, the action of acids on insoluble salts, contact action, the electrical method, and the inverting action of acids on sugar. The object in view was in all cases practically the same—to compare the influence exerted by different acids under the same circumstances, and thus to measure their specific coefficient of affinity.

(1) In the optical method the coefficient of refraction of various solutions is determined, and the change produced by mixing these solutions in certain ways, and thus it is possible to draw conclusions in regard to the character of reactions which take place in solutions.

(2) An illustration of the method involving the action of acids on insoluble salts will make the method clear. A weighed quantity of calcium oxalate is treated with equivalent quantities of different acids in dilute solutions, and the quantity of the salt dissolved then determined. From this it is possible to calculate the specific coefficients of affinity of the acids.

(3) The simplest method of all is the electrical. This consists in determining the conducting power of solutions of different dilutions. In this way figures are obtained which bear to one another the same relations as those expressing the coefficients of affinity.

For details in regard to these and the other methods used by Ostwald in his studies of affinity the student is referred to the original papers of this chemist, and to his masterly book "Allgemeine Chemie." It is sufficient for the present purpose to call attention to the general result that, when acids and bases are compared in many different ways, they are found to differ markedly from one another, and the order in which they are arranged by the results of the different methods is always practically the same.

CHAPTER XIX.

CONNECTION BETWEEN THE CHEMICAL CONSTITUTION AND PROPERTIES OF COMPOUNDS.

General.—In the chapter on constitution frequent reference was made to the fact that a certain constitution always carries with it certain properties. Thus all alcohols have certain common properties, and they have the same general constitution; and this is true of every other class of compounds. Besides this general connection, there are more special kinds which have not thus far been treated. These special kinds of connection may be conveniently considered under a few heads:—

(1) Change of character in certain parts of a compound caused by the introduction of some atom or group;

(2) Tendency on the part of certain compounds to break down in certain ways;

(3) Influence exerted by certain atoms or groups already in a compound on the constitution of the products formed by further acts of substitution;

(4) Relative ease with which isomeric compounds enter into action.

1. *Change of Character in Certain Parts of a Compound caused by the Introduction of some atom or Group.*

Bases, Alcohols, Acids.—These three classes of compounds illustrate very well the marked changes in properties which one part of a compound can undergo in consequence of changes in some other part. In the primary alcohol, $R—\underset{H_2}{\underset{\|}{C}}—O—H$, hydrogen is in combination with the carbon atom with which the hydroxyl is combined, and the substance has basic properties. When, however, the two hydrogen atoms of the group $—\underset{H_2}{\underset{\|}{C}}—$ are replaced by

oxygen, the hydroxyl hydrogen acquires entirely different properties. The compound $R—\underset{\underset{O}{\|}}{C}—O—H$ is an acid. Here, apparently, the hydroxyl remains in the compound as it was, but the carbon with which it is in combination, instead of being linked to hydrogen, as in the alcohol, is linked to oxygen. This power of oxygen to give acid properties to hydroxyl is also seen in aluminic acid, $OAl(OH)$, ferric acid, $O_2Fe(OH)_2$, and chromic acid, $O_2Cr(OH)_2$; and, indeed, in nearly all the common mineral acids, as $OP(OH)_3$, $O_2N(OH)$, $O_2S(OH)_2$, $OCl(OH)$, $O_2Cl(OH)$, $O_3Cl(OH)$, etc. In the case of any element it is true, with a very few exceptions, that that acid derivative which contains *the largest proportion of oxygen* has the most marked acid character.

Influence of Acid Groups like NO_2.—An influence similar to that referred to in the last paragraph is exerted in some cases by the acid residue, NO_2. This is seen in the acid character of the nitro-phenols and similar compounds. Phenol itself has very weak acid properties. It forms salts when treated with the caustic alkalies, but it has not the power to decompose carbonates. When, however, the hydrogen of the benzene ring is partly replaced by the nitro group the products formed have acid properties which are much more marked than those of phenol. Tri-nitro-phenol, $C_6H_2(NO_2)_3OH$, is a strong acid. A similar influence though less marked is exerted by chlorine and bromine.

The influence of the nitro-group on the hydroxyl group of the alcohols proper is not known, as nitro derivatives of these alcohols are not known. A remarkable influence is exerted by this group on hydrogen in direct combination with carbon. This is seen in some of the nitro-paraffins.

The compound $CH_3—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}—NO_2$ has acid properties. The acid character is strengthened by the introduction of bromine in the position indicated in the formula

to the benzene residue. So, too, there is a similar difference observed between the results obtained when the action takes place at the boiling temperature and at the ordinary temperature. In the former case the substitution is in the paraffin residue; in the latter it is in the benzene residue.

Oxidation Phenomena.—In general the paraffins are more easily broken down by oxidizing agents than the benzene hydrocarbons. If the residues of both these classes of hydrocarbons be combined in one compound, the paraffin portion is broken down by oxidizing agents, while the benzene portion is not affected. If a paraffin be oxidized alone the products are carbon dioxide and water. The simplest case is that of marsh-gas, CH_4. The changes involved in the conversion of this substance into carbon dioxide and water have already been treated (see *ante*, p. 155).

If a stable benzene residue be combined with methyl or any other paraffin residue, the latter breaks down tending to form carbonic acid, but as the benzene residue is not broken down the product of the oxidation is carbonic acid in which the group, C_6H_5, or phenyl is present in place of one of the hydroxyls:—

$$C\begin{cases} C_6H_5 \\ H \\ H \\ H \end{cases} \text{ is converted into } \quad C\begin{cases} C_6H_5 \\ O \\ OH \end{cases}.$$

If a second atom or group be introduced into benzene forming a compound of the general formula $C_6H_3\begin{cases} CH_3 \\ X \end{cases}$, the resistance of the paraffin residue to the influence of oxidizing agents depends upon the constitution of the product. It has been shown that when the group X is in the ortho-position relatively to the methyl an acid oxidizing agent like chromic acid does not change the methyl, this residue becoming under these conditions as stable as the benzene residue On the other hand, potassium permanganate oxidizes such a group without difficulty. If two paraffin residues are in a benzene compound and a substituting atom or group be in the ortho-position to one and not to the other, the latter is oxidized by chromic acid and the former is not. Potassium permanganate

oxidizes both. *If* the compound be treated with fusing caustic potash, the ortho-methyl is, however, first oxidized.

2. *Tendency on the Part of Certain Compounds to break down in Certain Ways.*

Anhydrides.—The phenomena included under this head are illustrated by the formation of anhydrides of acids of certain constitution. The simplest cases are those of carbonic acid and sulphurous acid; and the formation of ammonia from ammonium hydroxide is a reaction of the same kind. In the case of the formation of carbonic anhydride, it is said that one carbon atom cannot hold in combination more than one hydroxyl group. While most facts are in accordance with this statement, some are not. Thus it appears that in mesoxalic acid there is a carbon atom in combination with two hydroxyls, as represented in the formula $C(OH)_2 \begin{cases} CO_2H \\ CO_2H \end{cases}$. So, too, chloral hydrate probably has the constitution $CCl_3—CH(OH)_2$. From these facts it would appear that carbon, which is in combination with certain acid groups, can hold two hydroxyls in combination. The breaking down of sulphurous acid $SO_2 \begin{cases} H \\ OH \end{cases}$ into sulphur dioxide and water is similar to the breaking down of carbonic acid. But that sulphur can hold two and perhaps a larger number of hydroxyl groups in combination is shown in sulphuric acid, H_2SO_4 and in the acid $H_2SO_4 + 2H_2O = S(OH)_6$. Indeed, the two hydroxyls in the acid H_2SO_4 are, as is well known, held very firmly. So, too, nitrous acid, $ON.OH$, loses water, spontaneously forming the anhydride, N_2O_3, but nitric acid, $O_2N.OH$, does not break down by loss of water, the addition of oxygen in this case as in the case of sulphuric acid increasing the stability of the product. Facts of the same order are noticed in the seventh group of elements, and particularly clearly among the acids of iodine.

The loss of water and formation of acid anhydrides by the interaction of two hydroxyl groups not in combination with the same atom are illustrated in the case of pyrosulphuric acid and pyrochromic acid. The change in the

latter case takes place spontaneously, and, indeed, unless basic compounds be present, it is carried to the formation of chromic anhydride. Among the acids of silicon such changes are of special interest, as they give rise to the many forms of polysilicic acids. Among carbon compounds a connection has been established between the constitution of certain acids and the ease with which they give up water. The generalization which has been reached is this: When two carboxyl groups are in combination with carbon atoms which are in combination with each other, water is given off easily and an anhydride formed. This is illustrated by the case of succinic acid, $\begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$, which, when heated, loses water and is converted into succinic anhydride, $\begin{array}{l} CH_2.CO \\ | \\ CH_2.CO \end{array}\!\!>O$. In the aromatic series this phenomenon is of special interest. It is noticed that the ortho-dicarbonic acids, like phthalic acid, $C_6H_4\!<\!\begin{array}{l} COOH \\ COOH \end{array}$, in which, according to the commonly accepted hypothesis concerning the structure of benzene, the two carboxyl groups are in combination with carbon atoms which are linked together, it is noticed that such acids lose water easily, while the isomeric acids do not form anhydrides. Thus, ortho-phthalic acid yields the anhydride $C_6H_4\!<\!\begin{array}{l} CO \\ CO \end{array}\!\!>O$, while isophthalic and terephthalic acids do not yield anhydrides.

Lactones.—The formation of lactones (see *ante*, p. 220) by loss of water from the hydroxy-acids is an illustration of the same kind of action as that of the formation of acid anhydrides. It has been shown that the γ- and δ-hydroxy-acids are extremely unstable, breaking down into lactones and water when set free from their salts. Here, it will be observed, the position of the hydroxyl with reference to the carboxyl is of marked influence on the stability of the compounds.

Lactams and Lactims.—Among aromatic compounds containing the amido group those in which this group is in the ortho position relatively to a group containing carboxyl give up water in two ways as indicated in the two equations:—

$$C_6H_4\left\langle\begin{matrix} CO.COOH \\ \\ NH_2 \end{matrix}\right. = C_6H_4\left\langle\begin{matrix} CO - CO \\ \qquad\quad | \\ NH - \end{matrix}\right. + H_2O;$$

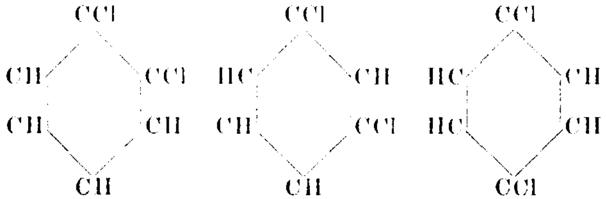
$$C_6H_4\left\langle\begin{matrix} CO.CO.OH \\ \\ NH_2 \end{matrix}\right. = C_6H_4\left\langle\begin{matrix} CO \\ \\ N \end{matrix}\right\rangle C.OH + H_2O.$$

The product of the first reaction is called a *lactam* and that of the second reaction is called a *lactim*. A condition of the formation of compounds like these is that the amido group must be in the ortho position relatively to the group containing the carboxyl.

Other Anhydro Compounds.—There are several other classes of compounds formed by loss of water in much the same way that anhydrides, lactones, lactams, and lactims are formed. Among these are the *sulphinides* which are formed by loss of water from ortho-sulphamine acids of the aromatic series. The simplest case is that of benzoic sulphinide, $C_6H_4\left\langle\begin{matrix} CO \\ SO_2 \end{matrix}\right\rangle NH$, which is formed from ortho-sulphamine benzoic acid, $C_6H_4\left\langle\begin{matrix} COOH \\ SO_2NH_2 \end{matrix}\right.$. The *anhydro bases* are formed whenever an acid residue is introduced into an ortho-diamido compound. Thus, when ortho-diamido-benzene is treated with glacial acetic acid, the product is a compound of the constitution $C_6H_4\left\langle\begin{matrix} NH \\ N \end{matrix}\right\rangle C.CH_3$. The formation is due to a loss of water from the compound $C_6H_4\left\langle\begin{matrix} NH.CO.CH_3 \\ NH_2 \end{matrix}\right.$, which in all probability is the first product of the reaction.

the hydrogen atoms in each of them bear the same relation to the molecule. The moment substitution has taken place in a symmetrical compound and a mono-substitution product is formed, the symmetry is destroyed, and, in all cases except that of marsh-gas, the second substituting atom or group may enter in more than one place. Thus when hydrogen in ethane has been replaced by chlorine, the unsymmetrical compound CH_3—CH_2Cl is formed. A second chlorine may enter either in the position indicated in the formula CH_3—$CHCl_2$ or in that indicated in the formula CH_2Cl—CH_2Cl. In mono-chlorbenzene chlorine may enter in three positions indicated by the formulas:—

I. II. III.



Some progress has been made in the investigation of these phenomena, and a few generalizations have been reached.

Influence of Acid or Negative Groups on Groups of the same Kind.—The most common case is that in which an acid atom or group enters a compound in which there is already an atom or group of the same kind. So far as this subject has been investigated in the paraffin series it appears that a second acid atom entering a compound tends to combine with the same carbon as that with which the first is combined. The same rule appears also to apply to the entrance of a third acid atom. Thus, by the action of chlorine, chlor-ethane, CH_3—CH_2Cl, is converted successively into CH_3—$CHCl_2$, CH_3—CCl_3, CH_2Cl—CCl_3, etc. The following are some of the general laws that have been found to govern substitution in the aromatic series:—

(a) When chlorine or bromine is present in benzene a second atom of either of these elements takes mainly the para-position, though there is always substitution to a slight extent in the ortho-position.

(b) A second nitro-group takes mainly the meta-posi-

tion with reference to the first, though to some extent it takes the ortho- and para positions.

(c) A second sulphonic acid group (SO_3H) takes mainly the para-position, but to some extent the ortho-position.

(d) Towards hydrocarbon residues like CH_3, C_2H_5, etc., acid groups tend to take the para-position. Ortho-compounds are formed in smaller quantity.

(e) Hydroxyl exerts in general the same kind of influence as methyl and other hydrocarbon residues.

(f) Carboxyl tends to make acid groups take the meta-position mainly, though in some cases the ortho- and para-positions may be occupied to some extent. When chlorine acts upon benzoic acid, meta-chlor-benzoic acid is apparently the only mono-substitution product formed; when sulphuric acid acts upon benzoic acid meta-sulpho-benzoic acid is the principal product, but there is formed at the same time a small quantity of the para-acid; and, finally, when nitric acid is the substituting agent the meta-acid is the chief product, and the ortho- and para-acids are formed in smaller quantity.

Influence of Basic or Positive Groups.—The ammonia residue NH_2 is the most common example of such groups. The influence of this group is such as to make an acid group take mainly the para- and meta-positions, and, to a subordinate extent, the ortho-position.

Other regularities besides those above mentioned have been observed, and the general subject of such regularities is under investigation. Still, we are only at the beginning of our knowledge in this direction, and much is to be hoped from a more careful study of substitution-phenomena from this point of view. The above statements are not all absolutely true, for in some cases the nature of the substitution products is found to differ according to the conditions under which they are formed. Thus, though, at ordinary temperatures the chief product of the action of sulphuric acid on phenol is the ortho-sulphonic acid, the para-acid being formed in small quantity; at a higher temperature only the para-acid is formed.

Regularities in the Addition of Negative or Acid Atoms to Unsaturated Compounds.—A kind of action similar to that treated in the last paragraph, though at the same time

methyl iodide, and represented thus:—

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CHNa \\ | \\ CO_2C_2H_5 \end{array} + ICH_3 = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH.CH_3 \\ | \\ CO_2C_2H_5 \end{array} + NaI.$$

The reaction was tried with methyl iodide, ethyl iodide, ethyl bromide, propyl iodide, and isopropyl iodide. The time required to effect complete transformation of molecular weights of these compounds in grams was:—

Methyl iodide,	4	minutes.
Ethyl iodide,	39	"
Ethyl bromide,	460	"
Propyl iodide,	162	"
Isopropyl iodide,	445	"

Similar experiments have been made with some of the same halogen derivatives and nascent hydrogen from different sources, with silver nitrate and with caustic alkalies. While the results cannot be stated quantitatively with any degree of confidence, one general result is of interest. It appears that: In acid solution ethyl and normal propyl bromides are most stable, and isopropyl bromide least so. In alkaline solutions, on the contrary, the reverse is true, that is to say, ethyl and normal propyl bromides are least stable, and isopropyl bromide most stable.

INDEX.

ACETONES, 152, 216
  methods of formation, 153
Acetoximes, 171
Acetylene, 236
Acid, *acetic*, 211
  acrylic, 236
  brompyromucic, 263
  butyric, 211, 213
  caproic, 215
  carbonic, 226
  chloric, 176
  chlorauric, 126
  chlorous, 176
  chlorplatinic, 126
  chromic, 197
  cinnamic, 263
  citric, 223
  cyanic, 224
  diethylacetic, 215
  dithionic, 183
  formic, 311
  glyceric, 222
  glycolic, 218
  hydracrylic, 219
  hydrazoic, 125
  hydrotiglic, 214
  hydroxyacetic, 218
  hydroxypropionic, 219
  a-hydroxypropionic, 219
  hypochlorous, 176
  hypophosphorous, 187
  isobutylacetic, 215
  isobutyric, 213
  isocaproic, 215
  isophthalic, 248, 250, 252
  isosuccinic, 221
  isovaleric, 214
  laevolactic, 219
Acid—
  malonic, 221
  mesitylenic, 252
  metaphosphoric, 191
  methylethylacetic, 214
  methylpropylacetic, 215
  nitric, 185
  nitrous, 185
  normal boric, 191
    caproic, 215
    silicic, 192
    valeric, 214
  orthoamidobenzoic, 263
  oxalic, 220
  oxybenzoic, 252
  paralactic, 219
  paroxybenzoic, 252
  pentathionic, 184
  perchloric, 176
  periodic, 176
  phosphoric, 188
  phosphorous, 187
  phthalic, 248, 252
  propionic, 211
  pyrochromic, 198
  pyromucic, 264
  pyrophosphoric, 190
  pyrosulphuric, 182
  salicylic, 252
  silicic, 192
  succinic, 221
  sulphocarbonic, 227
  sulphocyanic, 224
  sulphuric, 178
  sulphurous, 177
  tartaric, 223
  terephthalic, 248, 250, 252
  tetrathionic, 177, 184

Acid—
thiosulphuric, 182
trimesitic, 252
trimethylacetic, 214
triphenylcarbinol-carbonic, 262
trithionic, 183
uric, 228
uvitic, 252
valeric, 211, 214
xanthogenic, 227
Acids, 121, 146
avidity of, 295
classification of, 127
dibasic, 127
double halogen, 125
hydrogen, 121
hydroxyl, 121
metal, 197
methods of formation, 147
monobasic, 127
monohydroxy-monobasic, 218
nitrogen, 125
normal, 193
polysilicic, 192
sulphur, 124
tetrabasic, 127
tribasic, 127
unsaturated, 235
Acroleïn, 235
Affinity, chemical, 17, 291
co-efficients of, 298
distinction between, and valency, 91
measurements of, by observations on heat phenomena, 293
resultant, 294
rough measurements of, 291
specific co-efficient of, 300
Alcohol, active amyl, 206, 207
allyl, 234
ethylene, 216
isoamyl, 206
isobutyl, 205
isopropyl, 202
normal amyl, 206
normal butyl, 204
propyl, 202
pseudopropyl, 202
secondary butyl, 205
Alcohol—
tertiary butyl, 205
Alcohols, 140
diacid, 216
primary, 141
secondary, 142
tertiary, 144
triacid, 222
unsaturated, 234
Aldehydes, 149
Aldoximes, 171
Alloy, 31, 32
Allyl mustard oil, 225
Amido compounds, 172
Amines, 283
Ammonium, 195
chloride, specific gravity of vapor, 56
salts, 195
Ampère's hypothesis, 36
Amylbenzene, 246
Anhydrides, 130, 159, 307
Anhydro-bases, 309
Anhydro-compounds, 309
Anthracene, 270
Anthraquinone, 272
Arrhenius, 63, 64
Atomic hypothesis, 14
theory, 21
weights, determination of, 22
by analysis, 22
chemical decompositions, 29
substitution, 28
determined by isomorphism, 75
Atoms, 21, 38
linkage of, 117
number of, in molecules of elements, 41
Avidity of acids, 295
Avogadro's hypothesis, 37, 38
law, 39
views, 36
Azobenzene, 257
Azo-compounds, 255
Azoimide, 125
Azoxy-compounds, 259

Baeyer's views on benzene, 245
on ring compounds, 289

Bamberger, on naphthalene, 267
Bases, 127
complex, 129
Benzene, 238
prism formula of, 244
substitution products of, 246
Berthelot, 279
and St. Gilles, 298
Berthollet, 19, 296
Berzelius, determination of atomic weights by, 26
rules of, 27
Bonds of carbon atom, 283
Boyle's law, 38
Brühl, 278, 279, 286
Bunsen, on mass-action, 297
Butane, derivatives of, 202
normal, 203
Butylbenzene, 246
Butylcarbinol, 206
secondary, 206
Butyro-lactone, 220

Carbamide, 227
Carbamines, 164
Carbon, asymmetrical, 207, 220, 288
Carbon, sulphoxide, 227
Carbonyl chloride, 227
Chemical affinity, 17, 291
Chromium salts, 197
Chrysene, 272
Claus, on constitution of benzene, 245
Clausius, 63
Co-efficients of affinity, 298
Combining numbers, 21
Compound, chemical, 31
Compounds, 31
atomic, 94
molecular, 94
saturated, 99
unsaturated, 99
Constitution, definition of, 111
Copper salts, 195
Crafts, investigations on the specific gravity of the vapor of iodine, 47
Cyanamide, 224
Cyanides, 164
Cyanogen, 224
compounds, 224

Dalton, investigations of, 19
De Vries, on osmotic pressure, 63
Diazo-compounds, 255
Dichlornaphthoquinone, 266
Diethyl-carbinol, 206, 207
Diisopropyl, 208
Dimethyl-butyl-methane, 209
-diethyl-methane, 219
-ethyl carbinol, 207, 208
methane, 206
Diphenyl-methane, 260
phthalide, 261
Dipropargyl, 237
Dissociation in solutions, 63, 64
Dulong and Petit, investigations of, 66

Elements, 30
Equivalents, 24
Ethane, derivatives of, 200
Ethereal salts, 157
Ethers, 158
Ethylbenzene, 246
Ethylene, 234
chloride, 200

Faraday, on magnetic rotary polarization, 284
Fatty compounds, 199
Favre and Silbermann, 43, 279
Formula, constitutional, 116
empirical, 112
molecular, of gaseous compounds, 55
reaction, 115
structural, 116
synthesis, 115
Freezing-point of solutions, 61
Furfural, 264
Furfuman, 263

Gay Lussac, investigations of, 34
Glycerin, 222

Glycol, 216
Gravity, specific, of compounds in the form of vapor, 48–52
specific, abnormal, 55
Guldberg and Waage, 297, 298, 299, 300

Heat, molecular, 72
of formation, 280
of neutralization, 282, 295
specific, 65
of boron, 73
of carbon, 73
of silicon, 73
of vapor of mercury, 45
Heptane, derivatives of, 209
normal, 209
Hess, 279
Hexane, derivatives of, 208
normal, 208
Homologous series, 138
Homology, 138
Horstmann on mass-action, 297
Humpidge, 74
Hydrazine, 173
Hydrazines, 173
Hydrazo-compounds, 259
Hydrocarbons, constitution of, 136
normal, 139
Hydroquinone, 252
Hydroxylamine, 186
Hypothesis, 14
of Le Bel and van't Hoff, 220, 287

Imido-compounds, 172
Indigo-blue, 263
Iodine, changes by heat, 47
Iron salts, 197
Isatine, 263
Isobutane, 203
Isobutyl carbinol, 206
Isocyanide, 164
Isoheptane, 209
Isomerism, 201
Isomorphism, determination of atomic weights by means of, 75
Isonitriles, 164
Isonitroso-compounds, 171
Isopropyl carbinol, 205
Isoxylene, 252

Ketones, 216
Kopp on isomorphism, 76
Kundt on specific heat of mercury vapor, 45

Lactams, 309
Lactims, 309
Lactones, 220, 308
Le Bel, hypothesis of, 220, 287
Law:
of combination by volume, 34
of definite proportions, 14, 19
of indestructibility of matter, 14
of multiple proportions, 14, 19
periodic, 78
Linkage of atoms, 117
double, 102, 231
single, 102
triple, 102, 231

Magnetic rotary polarization, 283
Mariotte's law, 40
Mass-action, 296
Matter, constitution of, 21
Mechanical mixture, 31, 32
Meier and Victor Meyer on specific gravity of vapor of iodine, 47
Meier, F., and Crafts on specific gravity of vapor of iodine, 47
Mendelejeff on periodic law, 79
Menschutkin, 314
Mercaptans, 146
Mercury salts, 195
specific heat of vapor, 45
Mesitylene, 249, 253
Meta-compounds, 247
Metadibrombenzene, 252
Metadinitrobenzene, 252
Metamerism, 201

Metapicoline, 269
Methane, constitution of, 136
derivatives of, 199
Methylbenzene, 246
Methyldiethyl methane, 208, 209
ethyl carbinol, 205
propyl methane, 210
isopropyl carbinol, 207
mustard oil, 225
propyl carbinol, 206
Meyer, Lothar on periodic law, 86
Meyer, Victor, on specific gravity of vapor of iodine, 47
Mitscherlich, law of isomorphism, 75
Mixture, mechanical, 31, 32
Molecular rotary power, 284
weights, determination of, 39
Molecules, 37, 38
of elements with more or less than two atoms, 45
shape, of, 285
Mustard oils, 225

NAPHTHALENE, 248, 267
Nascent state, 54
Neumann on specific heat of compounds, 67
Neutralization, heat of, 282, 295
Newlands on periodic law, 78
Nilson, 74
Nitriles, 164
Nitro-compounds, 168
Nitrogen peroxide, specific gravity, 58
Nitroso-compounds, 171
Nitrous oxide, 185
Numbers, combining, 21

OILS, MUSTARD, 225
Ortho-compounds, 247
Orthodibrombenzene, 252
Orthodinitrobenzene, 252
Ortho-picoline, 269
Ortho-xylene, 252
Osmotic pressure, 61
Ostwald, 297, 299, 300, 301
Oxidation phenomena, 306
Oxides, 133
Ozone, proof that its molecule contains three atoms, 54

PARA-COMPOUNDS, 247
Paradibrombenzene, 252
Paradinitrobenzene, 252
Paraleucaniline, 261
Parapicoline, 269
Pararosaniline, 260
Paraxylene, 252
Pentane, derivatives of, 205
normal, 206
Periodates, 194
Periodic law, 78
Perkin on magnetic rotation, 284
Petit. See Dulong.
Petterson. See Nilson.
Pfeffer on osmotic pressure, 60, 62, 63
Phenanthrene, 272
Phenol-phthalein, 261
Phenols, 254
Phenylethylene, 262
Phenylmethane, 260
Phenylmethanes, 259
Phosphorus pentachloride, specific gravity of vapor, 57
Phthaleins, 261
Physical methods for determining constitution, 274
Physical structure, 275
Polarization, magnetic rotary, 283
Polymerism, 201
Propane, derivatives of, 201
Propylbenzene, 246
Propyl-carbinol, 204
Propylene, 234
Proust, investigations of, 19
Pyrene, 272
Pyridine, 268, 283
Pyrocatechin, 252
Pyrrol, 264

QUINOLINE, 268, 269
Quinones, 255

RAOULT, on solutions, 60
Refraction equivalent, 277

Refraction—
molecular, 277
Regnault, on specific heat of compounds, 67
Resorcin, 252
Ring-compounds, Von Baeyer's views on, 289
Rosaniline, 260
Rose on mass-action, 297

SALTS, 129
complex, 130
ethereal, 157
Selenium, varying number of atoms in molecule, 46
Silbermann. See Favre.
Solution, 31, 33
Solutions, laws of, 60, 61, 62
Stereochemistry, 289
St. Gilles. See Berthelot.
Structure, definition of, 111
Styrene, 263
Substituting groups, constitution of, 164
Substitution, 161
atomic in determining weights, 28
products complex, 163
containing chlorine, bromine, or iodine, 162
Succinic anhydride, 264, 308
Succinimide, 264
Sulphur dioxide, 176
trioxide, 176
varying number of atoms in molecule, 46

TETRAMETHYLETHANE, 208
methane, 206
Tetraphenylmethane, 260
Theory, 14
atomic, 21
of Guldberg and Waage, 271
Theory—
of types, 113
Thermal methods, 279
Thiophene, 265, 283
Thomsen, J., 279, 281, 282, 283, 299
Toluene, 246
Triethylmethane, 209
Trimethyl carbinol, 205
ethylmethane, 208
methane, 204
Triphenylmethane, 260
Types, 113
mixed, 113
theory of, 113

URANIUM-COMPOUNDS, 198
Urea, 227

VAN'T HOFF, hypothesis of, 220, 287
on solutions, 60, 62, 63
Valency, 88–110
apparent, 99
determination, 91
maximum, 99
periodic, variations in, 106
relative, 104
variations in, 94
Valylene, 237
Vapor-pressure of solutions, 60
Velocity of chemical change, 299
of formation of ethereal salts, 314
Volume, molecular, 275
specific, 275

WAAGE. See Guldberg.
Warburg. See Kundt.
Wollaston, 24, 25

XYLENES, 250

Remsen's Theoretical Chemistry—New (4th) Ed. Just Ready.

Principles of Theoretical Chemistry, with special reference to the Constitution of *Chemical Compounds*. By Ira Remsen, M.D., Ph.D., Professor of Chemistry in the Johns Hopkins University, Baltimore. Fourth and thoroughly revised edition. In one handsome royal 12mo. volume of 325 pages. Cloth, $2 00.

This work gives a brief and clear statement of the principles upon which the modern science of chemistry is based. The demand for four editions testifies not only to the intrinsic excellence of the work, but likewise to the growing appreciation of the fact that an understanding of the theory is a necessary foundation for a thorough working knowledge of chemistry.

Attfield's Chemistry—Twelfth Edition.

Chemistry, General, Medical and Pharmaceutical; Including the *Chemistry of the U. S. Pharmacopœia. A Manual of the General* Principles of the Science, and their application to Medicine and Pharmacy. By John Attfield, M.A., Ph.D., F.I.C., F.R.S., etc , Professor of Practical Chemistry to the Pharmaceutical Society of Great Britain, etc. A new American, from the twelfth English edition, specially revised by the author for America. In one handsome royal 12mo. volume of 782 pages, with 88 illustrations. Cloth, $2.75 ; leather, $3.25.

Attfield's *Chemistry* is the most popular book among students of medicine and pharmacy. This popularity has a good, substantial basis. It rests upon real merits. Attfield's work combines in the happiest manner a clear exposition of the theory of chemistry with the practical application of this knowledge to the every-day dealings of the physician and pharmacist. This last edition shows the marks of the latest progress made in chemistry and chemical teaching.—*New Orleans Medical and Surgical Journal*, November, 1889.

Simon's Manual of Chemistry—Third Edition.

Manual of Chemistry. A Guide to Lectures and Laboratory Work for Beginners in Chemistry. A Text-book, specially adapted for Students of Pharmacy and Medicine. By W. Simon, Ph.D., M.D., Professor of Chemistry and Toxicology in the College of Physicians and Surgeons, Baltimore, and *Professor of Chemistry* in the Maryland College of Pharmacy. New (third) edition. In one 8vo. volume of 477 pages, with 44 woodcuts and 7 colored plates illustrating 56 of the most important chemical tests. Cloth, $3.25. *Just ready.*

Vaughan & Novy on Ptomaines and Leucomaines—New (2d) Ed.

Ptomaines, Leucomaines and Bacterial Proteids; or the Chemical Factors in the Causation of Disease. By Victor C. Vaughan, Ph.D., M.D., Professor of Physiological and Pathological Chemistry and Associate Professor of Therapeutics and Materia Medica in the University of Michigan, and Frederick G. Novy, M.D., Instructor in Hygiene and Physiological Chemistry in the University of Michigan. New (second) edition. In one handsome 12mo. volume of 398 pages. Cloth, $2.25.

LEA BROTHERS & Co., Publishers, Philadelphia.

Stillé & Maisch's National Dispensatory—Fourth Edition.

The National Dispensatory. Containing the Natural History, Chemistry, Pharmacy, Actions and Uses of Medicines, including those recognized in the Pharmacopœias of the United States, Great Britain and Germany, with numerous references to the French Codex. By ALFRED STILLÉ, M.D., LL.D., Professor Emeritus of the Theory and Practice of Medicine and of Clinical Medicine in the University of Pennsylvania, and JOHN M. MAISCH, PHAR. D., Professor of Materia Medica and Botany in the Philadelphia Medical College of Pharmacy, Secretary to the American Pharmaceutical Association. Fourth edition revised, and covering the new British Pharmacopœia. In one magnificent imperial octavo volume of 1794 pages, with 311 elaborate engravings. Price in cloth, $7.25; leather, $8.00; half Russia, $9.00. ****This work will be furnished with Patent Ready Reference Thumb-letter Index for $1.00 in addition to the price in any of the above styles of binding.*

Maisch's Organic Materia Medica—New (5th) Edition. Just Ready.

A Manual of Organic Materia Medica: Being a Guide to Materia Medica of the Vegetable and Animal Kingdoms. For the use of Students, Druggists, Pharmacists and Physicians. By JOHN M. MAISCH, PHAR D., Professor of Materia Medica and Botany in the Philadelphia College of Pharmacy. New (fifth) edition, thoroughly revised. In one handsome royal 12mo. volume of 544 pages, with 270 illustrations. Cloth, $3.00.

A Text-Book of Practical Therapeutics—Second Ed.

A Text Book of Practical Therapeutics, with especial reference to the Application of Remedial Measures to Disease and their Employment upon a Rational Basis. By HOBART AMORY HARE, B.Sc., M.D., Professor of Materia Medica and Therapeutics in the Jefferson Medical College of Philadelphia, Secretary of the Convention for Revision of the U. S. Pharmacopœia of 1890. With special chapters by Drs. G. E. DE SCHWEINITZ, EDWARD MARTIN, J. HOWARD REEVES and BARTON C. HIRST. Second and revised edition. In one handsome octavo volume of 650 pages. Cloth, $3.75; leather, $4.75.

Brunton's Therapeutics and Materia Medica—Third Edition.

A Text-Book of Pharmacology, Therapeutics and Materia Medica; including the Pharmacy, the Physiological Action and the Therapeutical Uses of Drugs. By T. LAUDER BRUNTON, M.D., D.Sc., F.R.S., F.R.C.P., Lecturer on Materia Medica and Therapeutics at St. Bartholomew's Hospital, London, etc. Adapted to the U. S. Pharmacopœia by FRANCIS H. WILLIAMS, M.D., of Harvard University Medical School. Third edition. Octavo, 1305 pages, 230 illustrations. Cloth, $5.50; leather, $6.50.

LEA BROTHERS & Co., Publishers, Philadelphia.